

Uranium Series, Rates of Basaltic Melt Generation and Transport

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Synonyms

Basalt genesis; Mantle melting; Time scales of magmatic processes; Uranium-series isotope disequilibrium

Definitions

Uranium-series isotope disequilibrium. A state in which the activities (i.e., decay rates) of the short-lived daughter isotopes of radioactive ^{238}U or ^{235}U are different from their longer-lived parent isotopes in a geological sample due to a physical or chemical process (e.g., partial melting of the Earth's mantle) that changed the proportions of the elements of interest.

Magma. A molten, incandescent (hot), subterranean silicate fluid composed of melt and, in most cases, suspended mineral crystals and gas bubbles that may cool slowly within the Earth's crust to form an intrusive igneous rock or erupt at a volcano as lava or tephra.

Basalt. A mafic volcanic rock (lava) that forms when a magma with relatively high concentrations of magnesium and iron and a relatively low concentration of silicon (<52 wt% SiO_2) erupts onto the surface of the Earth.

Magmatic processes. The series of events that create and modify magma, including the generation of melt within the mantle and its modification prior to eruption due to crystallization, degassing, mixing, and/or assimilation of the surrounding rock.

Introduction

Short-lived uranium (U)-series isotopes are powerful tracers of the rates and mechanisms of basaltic melt generation and transport because their half-lives ($T_{1/2}$) are thought to be similar to the time scales of magmatic processes. The U-series isotopes that are most commonly applied to basalt genesis are ^{230}Th ($T_{1/2} = 75,700$ years), ^{231}Pa ($T_{1/2} = 32,800$ years), ^{226}Ra ($T_{1/2} = 1,600$ years), and ^{210}Pb ($T_{1/2} = 22$ years). The Earth's mantle (prior to melting) is generally thought to lie in a state of radioactive equilibrium in which the decay rates of these short-lived isotopes are equal to their long-lived, radioactive parents (either ^{238}U with $T_{1/2} = 4.5$ Gyr or ^{235}U with $T_{1/2} = 0.7$ Gyr). Magmatic processes, such as partial melting of the mantle, may change the relative proportions of these elements and create a state of radioactive disequilibrium between one or more parent-daughter U-series isotope pairs. Depending on the nature of the process involved, this elemental fractionation leads to a faster (relative) rate of decay for one of the isotopes in a pair. The isotope with a faster rate of decay rate is said to have an “excess” (e.g., excess ^{230}Th), whereas the isotope with a slower rate of decay is said to have a “deficit” (e.g., a deficit of ^{238}U). The magnitude of this disequilibrium in

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basalts is often a function of time-dependent phenomena, such as the rate of melt generation or the rate of mantle upwelling. In this summary, studies of U-series disequilibrium in basalts from three main tectonomagmatic environments are reviewed: mid-ocean ridges, intraplate oceanic volcanoes, and volcanic island arcs.

Mid-ocean Ridge Basalts

Mid-ocean ridge basalts (MORB) form due to partial melting of the uppermost mantle as a passive response to seafloor spreading. Young MORB display a wide range of negatively correlated ^{226}Ra - ^{230}Th and ^{230}Th - ^{238}U disequilibria with up to ~300 % excess ^{226}Ra and ~30 % excess ^{230}Th (e.g., Rubin and Macdougall 1988; Lundstrom et al. 1999; Sims et al. 2002). These signatures are thought to derive from the partial melting of the mantle over a range of depths (Lundstrom et al. 1999; Sims et al. 2002) at rates of solid mantle upwelling of ≤ 5 cm/year (e.g., Jull et al. 2002). Excesses of ^{230}Th and ^{226}Ra are likely created by a slow rate of melting at the bottom of the melting region in the stability field of garnet. The initial ^{226}Ra - ^{230}Th disequilibrium likely returns to radioactive equilibrium during melt transport through the mantle due to the short $T_{1/2}$ of ^{226}Ra , but the ^{230}Th excesses are preserved because much of the melt rises relatively quickly (relative to the $T_{1/2}$ of ^{230}Th) to the surface in chemically isolated channels (Lundstrom et al. 1999; Jull et al. 2002; Sims et al. 2002). In contrast, the final excesses of ^{226}Ra in MORB probably require the rapid extraction of melts that were recently in chemical equilibrium with the garnet-free top of the melting region, where no ^{230}Th excesses are produced (Lundstrom et al. 1999; Jull et al. 2002; Sims et al. 2002). The large excesses of ^{226}Ra in MORB constrain the maximum time scale from melting to eruption to be less than a few thousand years (Rubin and Macdougall 1988). However, deficits of ^{210}Pb (relative to ^{226}Ra) up to 15 % in zero-age MORB may require transport times from the source to the surface of only a few decades, if these ^{210}Pb - ^{226}Ra disequilibria are created during partial melting of the mantle (Rubin et al. 2005).

Intraplate Oceanic Basalts

Partial melting of the actively upwelling mantle at hot spots, such as the Hawaiian Islands (Pacific Ocean), Réunion Island (Indian Ocean), or the Galapagos Archipelago (Pacific Ocean), forms intraplate oceanic basalts. These melting anomalies are not directly tied to plate tectonics (unlike mid-ocean ridges and island arcs). Instead, this type of volcanism is thought to be related to the upwelling of mantle plumes that partially melt near the base of the oceanic lithosphere. A good example of intraplate oceanic basalts comes from the Hawaiian Islands, where a mantle plume is thought to be located under the Island of Hawai'i. This island comprises five volcanoes (Kīlauea, Mauna Loa, Mauna Kea, Hualālai, and Kohala), and a volcanically active seamount lies offshore (Lō'ihi). Unlike MORB, basaltic lavas from Hawaiian volcanoes possess relatively small ^{226}Ra excesses (up to only ~30 %) and variable ^{230}Th excesses that range from near equilibrium to MORB-like values up to 30 % (e.g., Sims et al. 1999; Pietruszka et al. 2001, 2011). The range in ^{230}Th - ^{238}U disequilibria for Hawaiian basalts is thought to be derived from a wide range in the rate of mantle upwelling and melting. The highest rates create the smallest ^{230}Th - ^{238}U disequilibria that are preserved in the lavas erupted near the central axis of the plume (Kīlauea and Mauna Loa). The lowest rates create the largest ^{230}Th - ^{238}U disequilibria that are preserved in lavas erupted from the margin of the plume (Lō'ihi, Hualālai, and Haleakalā, a volcano on the Island of Maui that was

active in recent prehistoric times). For example, the rate of mantle upwelling based on U-series isotope disequilibria is estimated to vary from up to 1,000 cm/year near the axis of the Hawaiian plume to ~5–6 cm/year near its margin (Sims et al. 1999; Pietruszka et al. 2001, 2011). This sort of zonation in the rate of mantle upwelling and melting for plume-derived lavas has also been observed in hot spot-related basalts from Iceland (Peate et al. 2001; Kokfelt et al. 2003). A general inverse correlation between ^{230}Th - ^{238}U disequilibria and inferred plume flux has been found for oceanic basalts from around the world (Chabaux and Allègre 1994; Bourdon et al. 2006).

Mafic Volcanic Rocks from Island Arcs

Mafic island arc magmas form at intra-oceanic subduction zones when aqueous fluids are released from the subducting slab (formerly altered oceanic crust) into the overlying mantle wedge, which leads to partial melting of the metasomatized upper mantle. Volcanic rocks from island arcs often have larger ^{226}Ra - ^{230}Th disequilibria (up to 500 %) than MORB or intraplate oceanic basalts (Turner et al. 2001) and an unusually wide range of ^{230}Th - ^{238}U disequilibria from up to ~30 % excess ^{230}Th to ~60 % excess ^{238}U (e.g., Elliott et al. 1997; Turner et al. 1997). The latter signature of excess ^{238}U (relative to ^{230}Th) is not found, even in small amounts, in the vast majority of MORB or intraplate oceanic basalts. The enrichments in ^{226}Ra and ^{238}U in island arc magmas are thought to result from the mobilization of these elements into slab-derived aqueous fluids (released during the dehydration of the subducting slab) and their introduction into the overlying mantle wedge prior to partial melting (e.g., Condomines and Sigmarsson 1993; Elliott et al. 1997; Turner et al. 1997; Sigmarsson et al. 2002; Bourdon et al. 2003; Dosseto and Turner 2013). The exceptionally large ^{226}Ra - ^{230}Th disequilibria preserved in young lavas from island arcs constrain the time scale of melt transport to only a few hundred years (from mantle source to surface), and the velocity of melt transport to ~1,000 m/year (Turner et al. 2001).

Summary

The U-series isotopic disequilibria of basaltic lavas allow the rates and mechanisms of basaltic melt generation and transport to be determined. These time-dependent phenomena, such as the rates of mantle upwelling or the time scales of melt transport beneath the active volcanic systems discussed above, would be difficult, if not impossible, to quantify using conventional geochemical tracers of the melt-generation process, such as stable, incompatible trace elements.

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Model Ages (Sm-Nd)

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Definition

A neodymium model age is an estimate of the age of “crustal formation” based on the assumption of a model composition for the mantle source. It is most commonly used to date the ages of crustal terranes within Precambrian orogenic belts or to estimate the provenance age of clastic sedimentary rocks.

Introduction

Nd model age dating is probably the most misunderstood of the major geological dating methods. As the name indicates, Nd model ages are dependant on a mantle model to determine ages, and their accuracy is therefore dependant on the suitability of the mantle model. Nd model ages also have relatively large analytical uncertainties of around ± 20 Myr. However, they are uniquely powerful in determining crustal formation ages, representing the time when crustal blocks were first created by mantle-derived magmatism, most commonly above subduction zones. In contrast, the U-Pb dating method provides much more precise and accurate ages for igneous crystallization, but can only provide a minimum age for crustal formation, since it cannot date the time of crustal separation from the mantle.

Historical Development

Nd model ages were conceived by DePaolo and Wasserburg (1976b), based on the observation by DePaolo and Wasserburg (1976a) that the initial ratios of terrestrial igneous rocks appeared to lie on the same Nd isotope growth curve as chondritic meteorites. Hence, they inferred that the mantle source of terrestrial igneous rocks had a uniform “Bulk Earth” signature equivalent to a Chondritic Uniform Reservoir (CHUR).

Since Nd and Sm are rare earth elements (REE) with very similar chemistry, it was inferred that within magmatic systems, these elements only undergo significant relative fractionation at low percentages of melting, such as when magmas are first extracted from the mantle. Since Nd is the more incompatible of the two elements, the process of “crustal extraction” or “crustal formation” leads to a markedly lower Sm-Nd ratio in crustal rocks relative to the mantle. In contrast, subsequent intra-crustal differentiation processes are not thought to cause significant further Sm-Nd fractionation. This leads to the scenario shown in Fig. 1.

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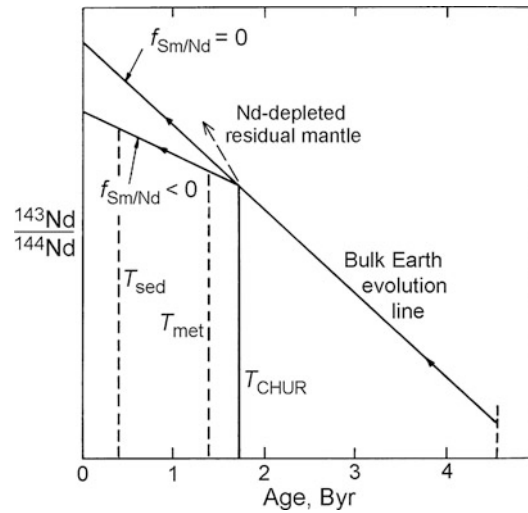


Fig. 1 Plot of Nd isotope evolution against time, showing the concept of Nd model ages based on the intersection of the isotopic growth line of the sample with that of the Bulk Earth, based on a chondritic model. McCulloch and Wasserburg (1978) and Dickin (2005)

The determination of the Nd isotope ratio and Sm-Nd ratio of a single crustal rock, presumed to have been an effectively closed system since crustal extraction, allows its Nd isotope growth line to be extrapolated back to its intersection with the CHUR evolution line, so that the point of intersection yields a T_{CHUR} model age for the analyzed sample. Algebraically, the age is defined as follows:

$$T_{\text{CHUR}} = \frac{1}{\lambda} \ln \left| 1 + \frac{\frac{(^{143}\text{Nd})^0}{(^{144}\text{Nd})_{\text{sample}}} - \frac{(^{143}\text{Nd})^0}{(^{144}\text{Nd})_{\text{CHUR}}}}{\frac{(^{147}\text{Sm})^0}{(^{144}\text{Nd})_{\text{sample}}} - \frac{(^{147}\text{Sm})^0}{(^{144}\text{Nd})_{\text{CHUR}}}} \right|$$

The non-deviation of the crustal growth line through metamorphic and sedimentation events in Fig. 1 is a schematic representation of the closed-system concept. Empirical evidence suggests that given an adequate-sized whole-rock sample of suitable chemistry, Sm-Nd systematics are resistant to high-grade metamorphism, even under severe deformation (e.g., Barovich and Patchett 1992). The Sm-Nd system may also remain unfractionated through erosion-sedimentation events, although the integrity of the system depends on the type and conditions of sedimentation. Clastic sediments have been shown to give good results, but chemical sediments have not (e.g., Bock et al. 1994).

In their pioneering demonstration of the Nd model age method, McCulloch and Wasserburg (1978) applied the model age dating technique to composite samples of the Canadian Shield, in order to achieve maximum coverage from a limited number of samples. They showed that Archean crust is preserved in several Proterozoic orogenic belts for which other dating systems (e.g., Rb-Sr and K-Ar) had been reset.

Problems with the chondritic earth model appeared when young oceanic volcanics were shown to deviate from the Bulk Earth composition, reflecting sources in the depleted upper mantle. It was realized that such a depleted mantle was an inevitable result of crustal extraction over earth history, leaving an incompatible-depleted residue with a higher Sm-Nd ratio than Bulk Earth (see vector in Fig. 1).

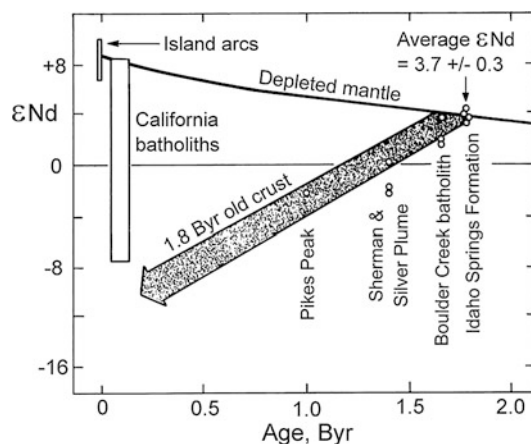


Fig. 2 Plot of Nd isotope ratio against time using the epsilon notation, which normalizes Nd isotope ratios relative to CHUR (epsilon Nd = part per 10,000 deviation from the CHUR line). The plot shows DePaolo's quadratic curve for depleted mantle evolution and the effects of subsequent intra-crustal melting to form granite batholiths such as Boulder Creek and Pikes Peak (After DePaolo (1981) and Dickin (2005))

To solve this problem, DePaolo (1981) derived an empirical model for a “depleted mantle” reservoir, which he believed would be typical of the asthenospheric “mantle wedge” that provides the source for subduction-related magmatism. He fitted a quadratic equation to three points to model this DM source: a chondritic source at 4.57 Ga, the juvenile Paleoproterozoic Idaho Springs Formation, and modern island arcs (Fig. 2). Although the model was ad hoc, the resulting T_{DM} ages have often yielded surprising accurate estimates of the crustal formation ages of major crustal blocks, when compared with other geochronological or geological evidence.

Controversies

Apart from the assumption of the mantle model and the closed-system assumption, the other major assumption of Nd model ages is that the crustal sample in question was extracted from the mantle during a single event. This is a good assumption for the formation of geological provinces such as the Superior Province of the Canadian Shield, which largely consists of a collage of accreted oceanic arcs (Hoffman 1989). However, continental margin arcs such as the Andes (ensialic arcs) are notorious for complex magmatic mixing of components with different ages (e.g., Mamani et al. 2010). If such samples are used to calculate Nd model ages, the result can be meaningless mixed ages (Fig. 3).

A warning against such mixed ages was given by Arndt and Goldstein (1987), in their notorious paper “The use and abuse of Nd crust formation ages.” The warning was perhaps necessary, because in their haste to characterize vast areas of continental crust with a very few Nd model ages, authors such as Nelson and DePaolo (1985) had cut corners and reached some erroneous conclusions. For example, they characterized the crustal formation age of the Penokean event as 2.3 Ga, based on a chance clustering of three Nd model ages with this value from Michigan. Unfortunately, the geological community became so obsessed by this warning that later estimates of crustal formation age would be questioned (e.g., Hanmer et al. 2000), even if based on much larger Nd data sets yielding consistent results.

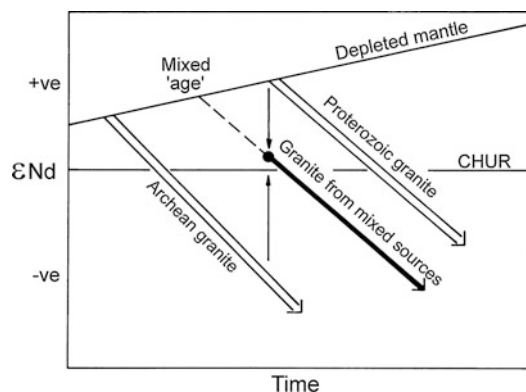


Fig. 3 Nd isotope evolution diagram using the epsilon notation, schematically showing the effects of Nd mixing to generate a composite sample whose Nd model age may not correspond with any real geological event (After Arndt and Goldstein (1987) and Dickin (2005))

Some Ground Rules for Future Work

In their critique, Arndt and Goldstein (1987) argued that Nd model ages should only be interpreted as true crustal formation ages “if they coincide with U-Pb zircon ages or other independent evidence of an orogenic event.” This is actually a misleading claim, which has led to additional confusion. An orogenic event is most often a collisional event and may not be a significant crust-forming event. A good example is the Grenville Orogeny, during which essentially *no* new crust was extracted from the mantle (Dickin et al. 2010). In such circumstances, large numbers of U-Pb ages may be generated that significantly post-date crustal formation (e.g., McNutt and Dickin 2012).

Ideally, if Nd model ages are used to determine the crustal formation age of accreted oceanic arc fragments (perhaps in a Precambrian crustal terrane), we may hope that U-Pb ages will be recovered that date igneous crystallization within the original arc. In that case, Nd model ages may coincide with U-Pb ages. However, even this scenario is oversimplified. The typical granitoid rocks that make up the bulk of the continental crust (tonalites and granodiorites) cannot be direct products of the mantle. When Nd model ages are determined on such material, they are probably dating their mafic crustal precursors, which may be millions of years older than the crystallization age of the plutons. Since it may take 50 Myr to create a mature island arc, we should expect that the Nd model ages for juvenile terranes may be 50 Myr older than the oldest U-Pb ages, which therefore provide only a *minimum* age for crustal formation. Therefore, if TDM model ages fall within 100 Myr or so of U-Pb zircon ages, this provides good evidence that we have a juvenile arc terrane (e.g., Daly and McLelland 1991).

If Nd model ages are more than 100 Myr older than the oldest U-Pb age, this may mean that an original accreted arc terrane was subsequently involved in a continental margin arc. Such arcs may generate pervasive magmatic reworking that almost completely masks the older crust-forming event. A good example is the 1.65 Ga Labradorian Orogeny of eastern Canada, which was partly established on an older 1.9 Ga Makkovikian accreted margin. For many years, the only evidence for the older event was the observation of ca. 2 Ga TDM model ages (Dickin 2000). However, pre-Labradorian U-Pb ages eventually confirmed the accuracy of the TDM ages as accurate estimates of the crustal formation age of the crust (Gower et al. 2008).

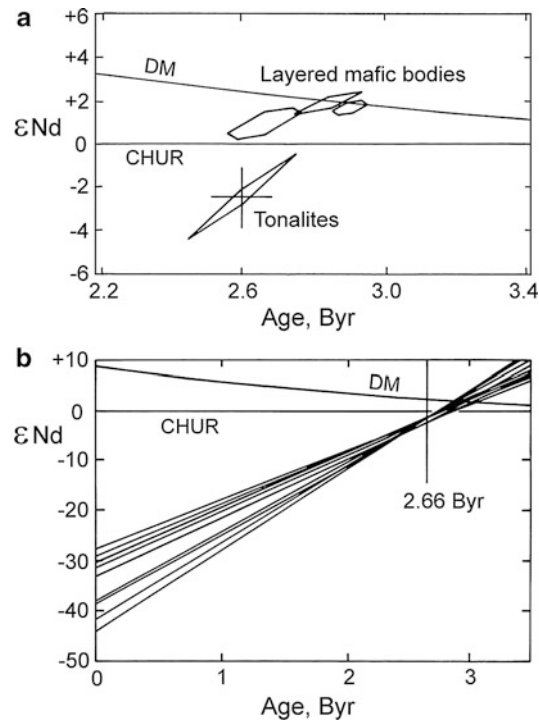


Fig. 4 Nd isotope evolution diagrams using the epsilon notation, showing data for the Lewisian gneisses of NW Scotland. **(a)** initial ratios for three isochron sets, **(b)** growth lines for individual samples comprising the tonalitic gneiss isochron (After Whitehouse (1988) and Dickin (2005))

Nd Model Ages and Isochron Ages

Contrary to popular belief, Sm-Nd isochrons are another valid way of testing Nd model ages. When a system is disturbed or mixed, it is unlikely that model ages and isochron ages will be affected in the same way. An illustration of these effects during high-grade metamorphism is shown in Fig. 4 (Whitehouse 1988). In this case, the Sm-Nd isochron age of Lewisian intermediate and granitic gneisses from NW Scotland was reset by high-grade metamorphism, causing the initial ratio of the isochron to lie off the DM line (Fig. 4a). However, the model ages of these rocks still approximately indicate their crustal formation age of 2.9 Ga (Fig. 4b), consistent with isochron ages for associated mafic gneisses.

An example where Nd model ages and isochron ages are consistent is provided by Mesoproterozoic gray gneisses from the Grenville province of Quebec. A suite of over 70 such gneisses from an area of nearly 100,000 km² gave a Sm-Nd isochron age of 1.51 $\pm$ 0.05 Ga and an average model age of 1.57 Ga (Dickin et al. 2010). These two ages are essentially within error and therefore validate the DM mantle model, suggesting that the suite represents a juvenile arc terrane extracted from the mantle over a few tens of millions of years around 1.5 Ga. This is confirmed by published U-Pb data within this terrane, yielding ages as old as 1.45 Ga (see references in Dickin 2000).

Conclusions

Nd model ages are uniquely powerful in providing an estimate of the formation age of Precambrian crustal terranes. They rely on geological assumptions and can therefore lead to erroneous ages if not correctly applied. However, given adequate sample sizes to test for effects such as mixing and disturbance, they can yield geologically accurate estimates for the time of crustal extraction from the mantle.

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Luminescence, Fluvial Sediments

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Definition

The use of luminescence techniques to determine the depositional age of sediments transported and deposited by rivers and other fluvial systems.

Introduction

Dating fluvial sediments with luminescence techniques has utility to a wide range of applications such as investigating fluvial processes and alluvial stratigraphy or dating fluvial sediments as proxies of climate, environmental and sea-level change, tectonic activity, and the age of archaeological sites. Thorough reviews of luminescence applications to fluvial sediments and the typical problems encountered in doing so are provided by Wallinga (2002), Jain et al. (2004), and Rittenour (2008). The earliest attempts to date fluvial sediments using luminescence were published by Murray et al. (1995). Since then, equipment and procedural advances, particularly the single aliquot regenerative dose (SAR) technique (Murray and Wintle 2000) and the ability to measure single grains (see Bøtter-Jensen et al. 2000), have improved the capability to measure multiple equivalent doses (D_e) from smaller and single grain aliquots quickly, thereby improving the ability to detect heterogeneous bleaching and to date fluvial sediments.

Heterogeneous bleaching (also referred to as partial or incomplete zeroing, or resetting) of the luminescence signals during transport is a common problem in the accurate determination of D_e in fluvial systems because of the attenuation of light through water and water-sediment mixtures. Fluvial sediments are particularly susceptible to type B partial bleaching (Duller 1994), in which grains in a sample are bleached to different degrees, resulting in significant scatter in the distribution of D_e and a high likelihood of overestimating of the true burial age. Contributing factors include varied modes of transport, whether by suspension, saltation, or bedload; rapid erosion associated with floods; and inputs from non-bleached and older deposits such as alluvial channel banks and beds, bedrock banks and beds, and the breakdown of larger clasts into sand sized and smaller particles through mechanical wear and abrasion during transport.

Although partial bleaching is likely in fluvial environments, some studies report well-bleached sediments evidenced by either strong agreement with independent age control or tightly clustered Gaussian D_e distributions (e.g., Murray 1996; Stokes et al. 2001; Kale et al. 2000; Kar et al 2001; Rittenour et al. 2003, 2005; Leigh et al. 2004). Possible explanations for well-bleached sediments in fluvial environments include transport during seasons or in systems with low turbidity and slack water or overbank deposition in environments where sediments may lay at the surface exposed to sunlight for some time after deposition before burial.

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In dating fluvial sediments, it is necessary to test for the presence of partial bleaching and, when present, to apply a strategy to determine the burial dose used in the final age calculation. Evidence of age overestimation owing to partial bleaching has been shown by measuring resetting rates as a function of attenuation of light in water, for example, in varied turbidity or transport distance; dating samples with independent age control; and dating modern samples (see Wallinga 2002; Jain et al. 2004 and references therein). Analytical approaches to identifying partial bleaching include examining the scatter in D_e distributions, comparing the form of different components of decay curves to isolate the most sensitive and well-bleached portion of luminescence signals, and comparing different luminescence signals, for example, by comparing TL and OSL results from a single sample (see Wallinga 2002 and references therein) or by comparing the differential bleaching rates of quartz and feldspar (Murray et al. 2012).

Approaches to determining the burial age from a population of D_e from a sample that has experienced partial bleaching include using small aliquots or single grains to isolate and disregard the partially and/or unbleached portion of the population of D_e and the application a variety of statistical methods (see Wallinga 2002; Rittenour 2008 and references therein). While using single grain aliquots is often the preferred method to cope with partially bleached samples, the use of small aliquots is statistically viable and more efficient in many situations. The luminescence signal from individual grains is highly variable, and in multiple grain aliquots of quartz, 90–95 % of the total light emitted originates from only 5–10 % of the grains (Duller et al. 2000; Jacobs et al. 2003). In those cases, small aliquots of < 100 grains are statistically equivalent to the single grain approach and improve the efficiency of analysis (Duller 2008). One approach is to test a small number single grains (e.g., one disk of 100 grains) to determine the percentage of grains that produce a luminescence signal and then adjust the number of grains per aliquot (i.e., the size of the aliquot) accordingly (e.g., Rodnight et al. 2006).

The use of single grains or small aliquots is particularly important for young samples (< 1 ka), and Jain et al. (2004) suggest that age offsets associated with partial bleaching are sufficiently masked by the analytical uncertainty associated with older samples. Nonetheless, heterogeneous bleaching has been observed in fluvial samples > 1 ka (e.g., Folz et al. 2001; Thomas et al. 2005; Brook et al. 2006; Srivastava et al. 2006; Eitel et al. 2006; Rodnight et al. 2006; Keen-Zebert et al. 2013), and disregarding the heterogeneously bleached condition can result in age overestimation greater than analytical error. Regardless of the expected age, an assessment of the degree of bleaching should be conducted taking into account the characteristics particular to each sample and site.

Samples with heterogeneous bleaching tend to have D_e populations with a wide range (high over-dispersion). Several statistical approaches to estimating burial doses have been posed including calculating the mean of the lowest 5–10 % of population of D_e (Olley et al. 1998), fitting the “leading edge” of the distribution after scatter from experimental errors is removed (Lepper et al. 2000), and fitting the distribution of D_e to statistical models such as the minimum age model (MAM) or finite mixture model (FMM) (Gailbraith et al. 1999; Galbraith 2005). For widely ranging, complex, multimodal distributions of D_e , for example, arising from fluvial sediment sources of mixed age, F-ratio filtering (a ratio of two independent estimates of the variance in a normal distribution) can be applied to discriminate between discrete populations within a distribution (Spencer et al. 2003; Spencer and Robinson 2008). In some partially bleached sedimentary environments, ages of samples in vertical succession may overlap owing to high over-dispersion and error. In these kinds of cases, rather than define a single age for a sample, it may be advantageous to define a probability distribution of ages from the population of D_e using a bootstrapping approach that enables the identification of trends in sedimentation rates down-

profile (Cunningham and Wallinga 2012). The choice of statistical approach to modeling the burial dose should be made according to the characteristics of the site, considering factors that contribute to large dispersion in the population of D_e such as partial bleaching, uneven dosimetry, and post-depositional mixing, for example, owing to bioturbation and other soil forming processes. Though inputting a smaller number of replicates of D_e into statistical models may be satisfactory for Gaussian distributions, for more complex distributions, such as those exhibiting high over-dispersion, at least 50–60 acceptable replicates of D_e may be necessary to generate reproducible results (Rodnight 2008; Woda and Fuchs 2008).

Current Gaps in Knowledge Related to Fluvial Processes

Early assumptions held that because fine grains are transported higher in the water column, they should be better bleached than coarser grains; however, studies have shown that coarser grains tend to be better bleached (Olley et al. 1998; Truelsen and Wallinga 2003; Hu et al. 2010). Although thermal transfer may be impacted by grain size, Truelsen and Wallinga (2003) suggest that better bleaching of coarse grains is not an artifact of thermal transfer effects related to grain size. Some possible explanations for this phenomenon include (1) channel bed armoring at lower flows or during receding flood flows in which finer sediments work into pore spaces in the bed through kinematic sorting leaving a coarser layer on top of the channel bed that would be exposed to sunlight during lower base flows; (2) for rivers with flashy and/or perennial flows, which are common in dryland rivers, equal mobility of all grain sizes during floods which would result in equal exposure to sunlight; (3) overbank sand dunes being deposited on the floodplain that are well exposed to sunlight then buried in subsequent flows; (4) fine sediment being transported as flocs (larger aggregates of fine sediment) the interiors of which would not be exposed to light during transport; and (5) in basins with heterogeneous lithology, differences in the source rock of fine and coarse fractions may give rise to fundamental differences in luminescence behavior or characteristics. These processes do not occur in all rivers, and other fluvial processes may contribute to a relationship between grain size and bleaching, but this phenomenon remains untested and more applications of luminescence could yield insight into fundamental fluvial processes related to grain size and transport.

Other issues associated with grain size and dating fluvial sediments relate to sorting, or the mixture of grain sizes within a landform or sample. Potential problems related to poor sorting (large variation of grain sizes within a feature) involve both the high potential for partial bleaching and uneven dosimetry, for example, from mixed fine, sand, gravel, and cobble sizes within a single feature such as a gravel bar. Outside of the findings of Murray et al. (1995) that floodplain deposits are better bleached than channel deposits, observations of the impact of sorting on luminescence ages are lacking.

A relationship between better bleaching with greater transport distance has been observed in some studies (Stokes et al. 2001; Pietsch et al. 2008; Summa-Nelson and Rittenour 2012). Though the phenomenon has not been thoroughly investigated in a variety of settings, possible explanations include increased sorting downstream, modification of grains during transport, and increased sensitivity owing to repeated bleaching and dosing cycles following detachment from the parent material through erosion and redeposition of sediment. More work is needed to validate these observations in other fluvial systems.

Some basic understanding about fluvial processes may be discovered through the use of portable OSL readers even though they are currently limited to measuring photon counts and do not enable

age determination. In particular, where multiple samples are collected across a gradient, insight on sedimentary characteristics may be discovered. For example, changes in sedimentological processes, variation in provenance, the likelihood of post-depositional mixing, and the suitability of sediments to dating with OSL can be assessed with photon counts from portable OSL readers (Muñoz-Salinas et al [2011](#)).

Recent Applications of Luminescence to Dating Fluvial Sediments That Have Independent Age Control

Historical and Sedimentary Age Controls

For case studies using historical information sedimentary stratigraphy, and radiocarbon as independent age controls, only publications that postdate Rittenour's review ([2008](#)) are presented here. On terraces on the Middle Thames with a chronology well-constrained by OSL, U/Th, and TL on artifacts, Pawley et al. ([2010](#)) found good comparison of quartz OSL with the expected 450 ka age of the site. Initial results found systematic underestimation of 10 % owing to contamination of the OSL signal by a thermally unstable medium component. The fast component was isolated by curve fitting and by early subtraction of the background, the latter of which was found to provide the best separation of the thermally unstable signal. For historical fluvial deposits on the Danube and Ebro, Fiebig et al. ([2009](#)) used 2 mm aliquots and the finite mixture model (FMM) on partially bleached sediments to find young ages (< 500 a) that were stratigraphically consistent and agreed with well-constrained chronologies from dendrochronology and archaeology at the site. In the hyperarid Negev, Porat et al. ([2010](#)) used the minimum age model on partially bleached sediments just underlying the abandoned surface of an alluvial fan and found good agreement between OSL and soil age estimates, morphostratigraphy, and well-dated lacustrine shorelines for the age of fan abandonment.

Radiocarbon

Because the applicable age range of luminescence overlaps that of radiocarbon, results from the two techniques are often used to validate each other. In comparing radiocarbon with OSL results and stratigraphic position in Holocene arroyo sediments in southern Utah, Summa-Nelson and Rittenour ([2012](#)) used both single grain and small aliquots of quartz to determine D_e distributions and the minimum age model to determine the burial dose used to calculate the age. They find good agreement within errors between OSL and radiocarbon results except for one sample that had no positive skew and low over-dispersion, and they suggest therefore that there was a problem with the dose rate estimation rather than with the determination of D_e . Very small aliquots (0.3 mm) were used with success by Cheetham et al. ([2010b](#)) to complete a Holocene alluvial chronology in southeastern Australia. Radiocarbon and OSL results were chronostratigraphically consistent, but for a few samples, evidence of bioturbation resulted in poor results from both techniques (Cheetham et al. [2010b](#)). Compared to the larger aliquots used by Cheetham et al. ([2010a](#)), results from the small aliquots used by Cheetham et al. ([2010b](#)) were more accurate, but were within two standard deviations of the earlier measurements of larger aliquots. Briant and Bateman ([2009](#)) conducted a cross-comparison of paired OSL and radiocarbon samples of fluvial sediments of the Nene and Welland rivers in eastern England and reconfirmed results of an earlier study (Briant et al. [2004a, b, 2005](#)) that had found offsets between OSL and radiocarbon results in older samples. In the later study, dose recovery tests and the SAR protocol were used on small (2 mm) aliquots to improve the confidence in the results of the earlier study that had used large aliquots, bringing into

question the possibility of partial bleaching. Reconfirming Briant et al. (2004a, b, 2005), the results show good age agreement between OSL and radiocarbon ages before 35 ^{14}C ka BP, but age underestimates by radiocarbon later (Briant and Bateman 2009). The authors attribute the result to the contamination of older organic material with modern carbon and suggest that confidence in conventionally pretreated radiocarbon ages be limited to < 35 ^{14}C ka BP.

Cosmogenic Radionuclides

Owen et al. (2006) and DeLong and Arnold (2007) compared OSL ages of alluvial sediments within fans to ^{10}Be cosmogenic radionuclide (CRN) exposure ages of boulders that were partially buried in alluvial fan surfaces. Both studies find good stratigraphic agreement among the methods, but acknowledge scatter in the CRN results owing to inheritance, post-depositional erosion and weathering, a limited number of CRN samples, and/or shielding. Hetzel et al. (2004) and Nissen et al. (2009) directly compared depth averaged ^{10}Be CRN ages to OSL ages of sediments within alluvial fans and found that OSL underestimated the ages, citing feldspar contamination and abnormal quartz characteristics. However, because the signal resetting mechanisms are fundamentally different (OSL being reset by exposure to light or heat and cosmogenic depth profiles being reset by a number of processes including sediment mixing, deep surface truncation, and inheritance), direct comparison of OSL and CRN ages is somewhat questionable (Guralnik et al. 2011). To cope with this discrepancy in resetting mechanisms, Guralnik et al. (2011) fit cosmogenic and luminescence data to a model that utilizes both OSL and CRN data to provide a more nuanced platform for interpretation of alluvial terrace history than is possible with results from one technique or from directly comparing both techniques on single sample sites.

Summary

Luminescence techniques can be used to date fluvial sediments for a variety of applications from understanding fluvial processes and alluvial stratigraphy to dating other landscape features. The high potential for partial bleaching prior to burial is the main concern regarding the accuracy and precision of luminescence ages of fluvial sediments. However, a combination of small aliquot or single grain techniques and the use of appropriate statistical models have yielded successful age determination of fluvial sediments with luminescence. Independent age dating techniques including historical ages, radiocarbon, and CRNs has repeatedly validated luminescence ages of fluvial sediments in a wide age range environmental settings and ages from the modern to the Pleistocene.

Cross-References

- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Geochronology](#)
- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Luminescence, Geomorphological Processes](#)
- ▶ [Luminescence Dating, Single Grain Dose Distribution](#)
- ▶ [Luminescence Dating, Uncertainties and Age Range](#)
- ▶ [Quartz](#)
- ▶ [Radiocarbon Dating](#)

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Luminescence, Colluvial Sediments

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Definition

Colluvium: sediment eroded from and transported along hillslopes by water, gravity, or human action and usually forms a wedge-shaped sediment body at the footslope.

Hillslope deposits are important sedimentary archives for geomorphological, paleoenvironmental, and increasingly also archaeological research. Besides others, they are utilized for reconstructing landscape response to climate change (e.g., Hanson et al. 2004), anthropogenic-induced soil erosion (e.g., Lang 2003), and fault activities (e.g., Fattahi et al. 2006). Various definitions for the term colluvium are in use in different scientific communities. In general, the term describes sediments that are eroded from and transported along hillslopes by running water or gravity and that usually form wedge-shaped deposits on the footslope. Typically, colluvial sediments are formed through processes on slopes that are spatially diffusive and are distinguished from alluvial sediments, which are transported across slopes in spatially confined channels to form alluvial fans and cones. The recent research focus on colluvial systems is linked to the limited transport distance within such systems and their reduced complexity that often allows cause-consequence analyses of sediment formation.

Luminescence dating determines the time when sediments were formed if sufficient exposure to daylight (bleaching) immediately before burial occurred. The potential of using luminescence for dating colluvium has already been explored by Forman et al. (1991) using thermoluminescence (TL). Wintle et al. (1993) were the first to report successful infrared-stimulated luminescence (IRSL) dating of colluvial sediments; later also optically stimulated luminescence (OSL) has been utilized for dating colluvium (e.g., Fuchs et al. 2004). For luminescence dating of colluvial sediments, limitations exist that are related to (i) limited bleaching due to limited exposure of sediment grains to daylight during the short and often rapid transport of slope deposits and (ii) low-luminescence sensitivity of quartz in many lithologically immature deposits:

1. Several processes are involved in eroding and transporting sediment along slopes, like sheet, rill and gully erosion, mass movements (e.g., debris flows, sliding, falling), and soil creep (e.g., solifluction). While these processes act on hillslope material to move it downslope, the sediment itself may move as a rigid block as in the case of sliding. Thus, in respect of exposure to daylight, only a small fraction of sediment grains involved in the process (e.g., only the outside layer of sediment grains on a rigid block) may be exposed to daylight. If material is transported in suspension, the intensity and spectral composition of the daylight is subdued by the suspended load. Also, many high-magnitude slope processes erode the material that they are moving across and incorporate unbleached material from the subsurface in the colluvial deposit they leave behind.

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Catchment morphology and erosion process constrain the sediment pathway, sediment travel distance, and sediment sink. Because travel distance is usually rather short, the probability of efficient bleaching is reduced and events may occur fully during unfavorable daylight conditions (e.g., transport entirely at night). In addition, a large variety of sediment source materials exist, leading to a large variety in sediment characteristics, e.g., grain-size distribution, mineral composition, or organic content. Some of these sediments tend to be transported as single mineral grains, like well-sorted dry sand, while others are prone to coagulation, like clay-dominated sediments. The latter often hampers sufficient zeroing of the luminescence signal, because the inner grains of an aggregate are shielded from daylight exposure (Lang 1994). The same may result from mineral coatings, where, e.g., iron, manganese, or carbonate coatings hamper the daylight to penetrate into the mineral grains.

2. As in other sedimentary environments, the use of quartz OSL in colluvial deposits can be hampered by poor luminescence sensitivity. Often materials incorporated in colluvium are freshly eroded from bedrock and enter the erosion-transport-deposition cycle for the first time. Quartz from such environments usually displays rather low-luminescence sensitivity as that seems to increase only after repeated cycles of sediment recycling (Pietsch et al. 2008).

Despite the shortcomings, there are many examples where luminescence dating of colluvium has successfully been carried out (for reviews, see Lang 2003; Fuchs and Lang 2009). Two factors influence this: (a) hillslope sediments are often eroded, transported, and accumulated not in a single event but temporary storage on the hillslope occurs, before a further mobilization takes place (e.g., Lang and Hönscheidt 1999). This increases the probability of exposure to daylight and thus bleaching. (b) Bioturbation and mechanical processes in the soil as well as cultivation allow that mineral grains are frequently exposed to daylight before the sediment grains are eroded. In many cases exposure to daylight continues after deposition until the sediment grains are covered through further sedimentation. According to Berger and Mahaney (1990), this process is more important for sediment bleaching than the colluvial transport itself. Nevertheless, as in other sedimentary environments, detecting and excluding insufficient bleaching is a necessary prerequisite for successful luminescence dating of colluvial sediments. This is demonstrated by some investigations of modern colluvial sediments, where residual luminescence signals were identified, which would result in age overestimations of hundreds (Yanchou et al. 2002) or even thousands of years (Porat et al. 2001). The large variety of sedimentary process and regional and climatic settings, however, make generic statements difficult: single-grain dose distributions by Vandenberghe et al. (2009) derived from fault scarp colluvium are unimodal, rather narrow, and are only slightly skewed, indicative of sufficient bleaching which is also confirmed by comparing the resulting OSL ages with independent age information. Porat et al. (2009) use OSL to date colluvial sediments from Eilat, southern Israel. Based on single-grain OSL measurements of quartz, they are able to identify bleached grains and manage to establish a chronology spanning the interval 1,300 years to 500 years ago. As in other sedimentary environments, and where possible, the analyses of dose distributions of single grains and small aliquots seem crucial also in colluvial deposits.

Conclusions

Due to rather restricted bleaching possibilities, colluvial sediments are challenging for OSL dating. Issuing generic statements on the suitability is difficult as colluvial sediments exist in a great variety in very different environments. It has been demonstrated that OSL dating is possible in

many cases; but success is often difficult to judge and success at one location does not guarantee success elsewhere. To establish a trustworthy and robust OSL chronology, internal (e.g., stratigraphic integrity) and external (e.g., accordance with independent information) consistency is a requirement.

Cross-References

- [Feldspar Infrared Stimulated Luminescence](#)
- [Luminescence Dating](#)
- [Luminescence Dating of Archaeological Sediments](#)
- [Luminescence Dating, Dose Rate](#)
- [Luminescence Dating, Single Grain Dose Distribution](#)
- [Luminescence Dating, Uncertainties and Age Range](#)
- [Luminescence, Earthquake and Tectonic Activity](#)
- [Luminescence, Fluvial Sediments](#)
- [Luminescence, Geomorphological Processes](#)
- [Luminescence, Soils](#)
- [Optically-Stimulated Luminescence \(OSL\)](#)
- [Radiation Dose Rate](#)
- [Sediments, Archaeological](#)

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Fission Track Dating and Thermochronology

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Definitions

Fission Track	A linear trail of radiation damage in an insulating solid resulting from the passage of fission fragments formed by spontaneous or induced fission of a heavy nucleus, especially of isotopes of uranium.
Fission Track Dating	A technique for geological or archaeological dating based on the accumulation of fission tracks from the spontaneous nuclear fission of ^{238}U in natural minerals and glasses.
Fission Track Density	The number of fission tracks counted per unit area on a given surface.
Fission Track Length	The length of a fission track measured under a microscope after chemical enlargement.
Fission Track Annealing	The property of fission tracks that results in the gradual repair of the radiation damage in the host material upon exposure to elevated temperatures.
Fission Track Analysis	The measurement of different fission track parameters including track density and track length that are used to monitor the degree of fission track annealing for the purpose of reconstructing rock thermal histories.
Fission Track Thermochronology	The reconstruction of rock thermal histories based on the fission track annealing properties of one or more constituent minerals.

Introduction

The use of accumulated radiation damage tracks from spontaneous nuclear fission in natural minerals was first suggested more than 50 years ago as the basis for a geological dating technique by Price and Walker (1963). Since that time fission track analysis has evolved to serve a range of geological, and occasionally archaeological, dating applications, with particularly widespread utility in the field of thermochronology. In this approach, the unique characteristic of fission tracks to fade, or anneal, at elevated temperatures is used to obtain both time and temperature information. The development of powerful modelling techniques now allows for reconstruction of the thermal histories of rocks by analysis of fission tracks in their constituent minerals. Fission track analysis has therefore emerged as one of the most important methods for thermochronology, especially in the low-temperature ($<150\text{ }^{\circ}\text{C}$) environment characteristic of approximately the upper 5 km of the Earth's crust.

Fission tracks were first observed by transmission electron microscopy as linear trails of radiation damage in mica by Silk and Barnes (1959) and Price and Walker (1962). These tracks appeared as cylindrical regions of highly disordered or amorphous material averaging around 10 nm across within an undisturbed crystalline matrix. Price and Walker (1963) went on to show that these tracks

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could be enlarged by a simple chemical etching treatment so that they could then be observed much more conveniently under an optical microscope. They also showed that many natural micas had a background of tracks from the spontaneous fission of ^{238}U and suggested that this was the basis for a new geological dating method. The simplicity of revealing fission tracks by etching led to a rapid expansion of activity by many researchers that explored the application of fission tracks, and other nuclear particle tracks, in many different branches of science as summarized by Fleischer et al. (1975). Of these, fission track dating has proved to be by far the most important.

Early work on fission track dating showed that fission tracks could be observed in a variety of natural minerals and glasses (for a review, see Wagner and Van den haute 1992), but most of these contain insufficient uranium or are too rare to be useful in routine dating studies. The pioneering studies by Naeser (1967) and Wagner (1968) focused attention on commonly occurring, uranium-bearing accessory minerals such as apatite, titanite, and zircon. These accessory minerals occur as trace constituents in a wide variety of common igneous, metamorphic, and sedimentary rocks and mostly contain suitable amounts of uranium within their structures (typically in the ppm to hundreds of ppm range) to be useful for fission track dating. Of these minerals, just one, apatite, has come to account for more than 80 % of all fission track analyses because of its common occurrence, generally suitable uranium concentration, consistent etching properties, and well-understood thermal annealing behavior.

The use of a particular mineral for fission track dating requires estimates of three quantities: (1) the number of fission tracks in the material, (2) the amount of fissionable parent isotope present, and (3) the rate of spontaneous fission decay. In addition, it must either be assumed that no fission tracks have been lost since the system was formed or that the degree of loss can be estimated. It was soon recognized, however, that fission tracks could undergo annealing if exposed to elevated temperatures, resulting in fission track ages that were “too young” compared to independent formation age estimates. Considerable effort was therefore devoted to understanding and quantifying this fission track annealing process, initially with the objective of “correcting” the observed ages in order to recover the true age of the material. Such attempts resulted in some success, particularly in dating natural glasses, such as tektites (Storzer and Wagner 1969).

It was soon realized, however, that this concept could be turned around so that fission track annealing could be used to recover information about the conditions of annealing rather than being used to correct ages. The three American physicists who originated the fission track method, Fleischer et al. (1965a, p. 389), observed: “As in all age measurements, one must ask what time interval is being measured. It is our opinion that the “low” ages which are sometimes obtained by the fission-track method represent definite physical events, such as heating episodes.” This was one of the key insights that initiated the study of thermochronology – the use of temperature-sensitive dating methods to reconstruct rock thermal histories – a field that has come to dominate the use of fission track analysis over the last 30 years.

The basic principles and applications of fission track dating and thermochronology have been extensively reviewed by Wagner and Van den haute (1992), Gallagher et al. (1998), Gleadow et al. (2002), Donelick et al. (2005), and Tagami and O’Sullivan (2005).

Spontaneous Fission and Nuclear Track Formation

Spontaneous nuclear fission is one of the rarest forms of radioactive decay and occurs naturally only in the isotopes of uranium and thorium. In practice, however, only ^{238}U is responsible for the fission tracks observed in natural materials, for which the spontaneous fission half-life is approximately

8×10^{15} years. Other isotopes of these heavy elements, ^{235}U and ^{232}Th , can effectively be ignored as a source of fission tracks because they are either much less abundant or have significantly longer half-lives. Even in ^{238}U , the rate of spontaneous fission decay is vastly slower than the normal alpha decay mode, so that only about one in every two million decay events in this isotope is the result of nuclear fission. The much more common alpha decay is the basis for three other dating methods (see “► [Uranium–Lead, U-Series, and U–Th:He Dating](#)”).

Spontaneous fission results in a great variety of middle-weight isotopes as daughter products, most of which are extremely difficult to measure due to the rarity of these decay events. However, fission track dating is extremely sensitive as it measures the *effect* of the decay in the form of radiation damage, rather than the decay products themselves. Each fission track represents a single ^{238}U nucleus that has decayed in this way, so that counting fission tracks is equivalent to counting individual radioactive decay events.

In spontaneous fission the parent ^{238}U nucleus splits apart into two sub-equal and massively charged particles that carry away most of the enormous energy released by nuclear fission as kinetic energy. These massively ionizing particles travel rapidly apart at 180° to each other, to produce a single linear trail of radiation damage in the host material, the fission track (see “► [Radiation Defect](#)”). The result is a narrow track core of amorphous material about 5–10 nm across but continuing for lengths of up to 20 μm in some materials. In apatite, recent evidence suggests that the track core may even be a void (Li et al. 2012).

Revealing and Observing Fission Tracks

Fission Track Etching

Fission tracks are revealed for counting and measurement under a microscope by a chemical etching procedure. The etchant preferentially attacks the damaged core of the track, which is chemically more reactive than the surrounding undamaged matrix. This contrast in reactivity is to be expected in crystalline minerals but also exists to a lesser degree in natural glasses, where the track core is more disordered than the surrounding glass matrix.

Etching is typically carried out on an internal surface of the material to be dated. Internal surfaces are exposed either by grinding and polishing or by exploiting the natural cleavage of minerals such as mica. The surface is immersed in a suitable chemical etchant for the particular mineral to enlarge latent fission tracks to optical dimensions of $\sim 1\text{--}2\ \mu\text{m}$ across.

Initially, etching of the track core is controlled by the radiation damage itself, but further enlargement of the track is controlled by the properties of the material. In the case of etching tracks in glasses, the rate of etching along the track is only slightly faster than the bulk etching rate of the surrounding material, so that the track is simultaneously widening while the etchant is still penetrating toward the end of the track. The outcome is a broad, conical-shaped track. In minerals, the etchant penetrates almost instantaneously along the whole length, so that the track subsequently widens as a nearly parallel-sided hole. As the etching rates are not uniform in different crystallographic directions, fully etched tracks are essentially faceted “negative crystals” forming shapes like knife blades, daggers, prisms, and pyramids depending on their orientation (Fig. 1). Figure 2 shows the appearance of well-etched tracks on a c-axis-parallel surface in an apatite crystal.

Prior to etching, minerals are typically separated from their host rock by crushing and then using standard heavy liquid and magnetic separation techniques, before mounting the concentrated mineral grains in a suitable medium such as epoxy resin or, for use with highly reactive etchants, transparent FEP teflon. Some typical etching treatments for different materials are listed in Table 1.

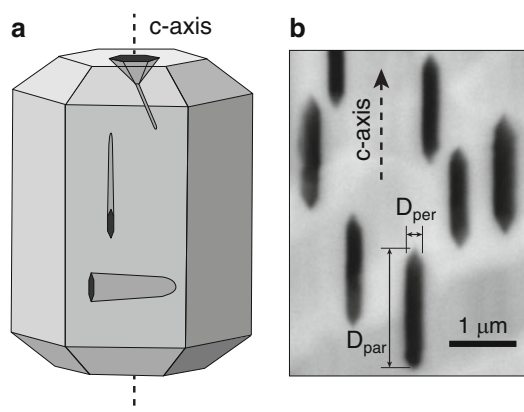


Fig. 1 The shape of etched fission tracks on different crystal surfaces in apatite (a). The scanning electron microscope image (b) shows the elongated appearance of etched fission track openings on a surface parallel to the c-axis. The long and short axes of etch pits are known as D_{par} and D_{per} (Donelick et al. 2005)

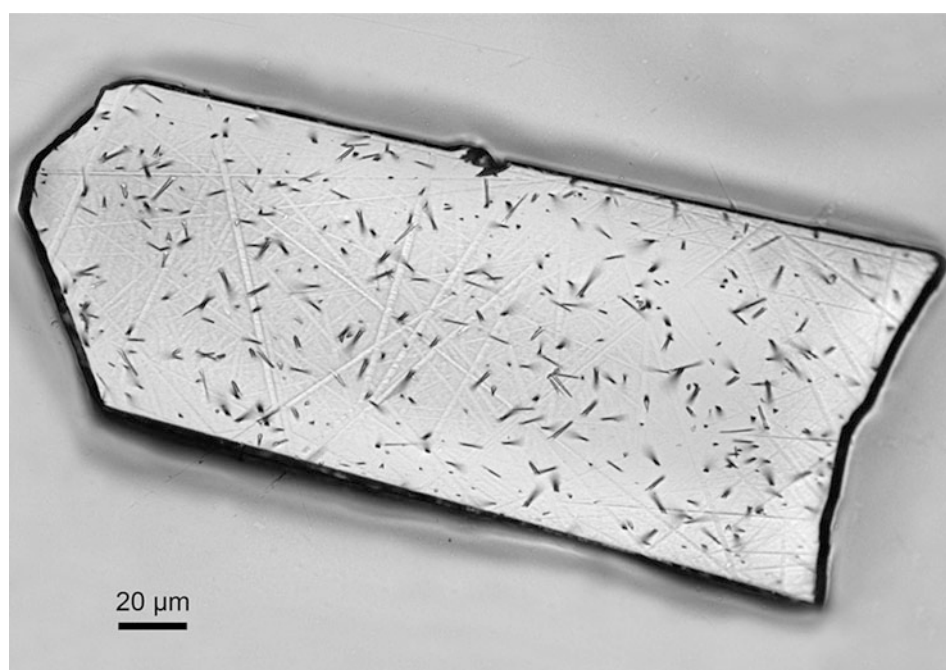


Fig. 2 Etched spontaneous fission tracks in an apatite grain from the Grassy Granodiorite, King Island, in southeastern Australia. The tracks appear as dark, randomly oriented lines of up to about 15 μm length. Faint lines running continuously across the surface are etched polishing scratches

Table 1 Commonly used etching conditions for revealing fission tracks

Mineral	Etchant	Temperature	Time
Apatite	5 N HNO_3	20 $^{\circ}\text{C}$	20 s
Zircon	KOH:NaOH eutectic	220 $^{\circ}\text{C}$	4–100 h
Titanite	50 N NaOH	120 $^{\circ}\text{C}$	30 min–5 h
	1HF:2HCl:3HNO ₃ :6H ₂ O	20 $^{\circ}\text{C}$	1–25 min
Muscovite mica	HF (40 %)	20 $^{\circ}\text{C}$	20 min
Natural glasses	HF (48–15 %)	20 $^{\circ}\text{C}$	15 s–5 min

Fission Track Microscopy

Observation and measurement of fission tracks requires a high-quality research microscope typically configured for illumination by both transmitted and incident light, a rotating nosepiece with various objectives up to $100\times$ with an appropriate substage condenser and a motorized x-y scanning stage. Track lengths are conventionally measured using a drawing tube device that superimposes an image of a digitizing tablet on the visible image, although modern equipment generally uses digital cameras attached to the microscope for this purpose (see section “[Automation of Fission Track Measurements](#)”).

The choice of objectives is important for fission track analysis and all objectives should be corrected for slides with no cover glass. Most researchers prefer to use dry objectives, rather than oil immersion lenses, especially for observation of fission tracks in apatite and mica whose refractive indices are almost the same as the immersion oil making the tracks difficult to see. Oil immersion lenses are, however, sometimes used for observing tracks in higher refractive index minerals, such as zircon and titanite.

The number of fission tracks present on a particular surface is most commonly counted at a magnification of $1,000\times$ or more by scanning across a calibrated grid of known area in the microscope eyepiece and recording the number of tracks with a hand tally device. In modern systems, digital cameras attached to the microscope generate a calibrated live image that can be analyzed directly on a computer, allowing counting of more complex regions of interest and marking of tracks on screen using a computer mouse. Digital image analysis may also be used as discussed below (see section “[Automation of Fission Track Measurements](#)”).

Fission Track Measurements

Measurements of fission tracks fall into two categories – counting the number of etched fission tracks intersecting a prepared surface and measuring various dimensions of the etched tracks. These two types of measurements respectively contain the time and the temperature components that are required for thermal history reconstruction.

Track Counting

The primary parameter measured in fission track analysis is the track density, which provides an estimate for the number of fission events accumulated over time in a geological material. The fission track density is defined as the number of track intersections per unit area of a given surface, usually expressed as tracks per cm^2 . As such, the track density is a two-dimensional measurement, which is related to the three-dimensional distribution of fission events via the average length of the fission tracks in that material.

Due to the anisotropic etching properties of minerals (see section “[Fission Track Etching](#)”), track densities are usually measured on specific crystal planes. In apatite and in zircon, the optimum surfaces for counting fission tracks are those that are cut parallel to the crystallographic c-axis. Such surfaces reveal tracks with a well-developed form and a high detection efficiency, which may be defined as the number of tracks actually counted as a function of the total number of tracks crossing that surface. In mica the optimum surface is the basal cleavage plane.

Track densities are of two kinds, spontaneous and induced. Spontaneous, or fossil, track densities record the number of tracks originating from spontaneous fission of ^{238}U contained within the target material. These are the fission tracks that accumulate over the geological lifetime of the material, their number being proportional to the time over which that accumulation has been taking place, and

the uranium concentration. Induced track densities, on the other hand, record the number of tracks arising from neutron-induced fission of ^{235}U and are used during fission track dating as a proxy for the amount of ^{238}U present in a sample (see section “[Fission Track Methods](#)”).

In determining the track density, it is important to reliably discriminate true fission tracks from non-track features such as dislocations, etching artifacts, inclusions, surface dust, and scratches. In most cases, the tracks are obvious and discrimination is straightforward, but occasionally very difficult grains with complex dislocation swarms are encountered. Such grains are best avoided altogether. Three commonly used criteria to discriminate tracks from non-track features are as follows: Fission tracks are straight-line defects, are randomly oriented, and are of limited length, determined by the range of fission fragments in that particular material (Fleischer and Price 1964). Dislocations and other spurious etch pits, on the other hand, are often preferentially oriented in parallel arrays, may be much longer than fission tracks, and often show complex curvature and branching paths. Interference from some of the other artifacts can be minimized by clean handling and careful observation.

Track Length Measurements

A second group of measurements relates to the overall dimensions of fission tracks, which can give valuable information on the degree of thermal annealing they have experienced. Different dimension parameters that have been used include the diameter of track etch pits in glasses, the projected lengths of tracks in minerals (the apparent length of dipping tracks projected onto the horizontal surface), and the lengths of confined fission tracks.

Most fission track studies in minerals since the mid-1980s have measured the lengths of horizontal confined tracks, especially in apatite (Gleadow et al. 1986). Confined fission tracks are tracks with their entire etchable length contained within the body of the surrounding mineral. In this case, the etchant penetrates into the confined track, not directly from the surface but from a surface-intersecting track or fracture. Depending on the way they are etched, confined tracks can be either track-in-track events (TINTs) or track-in-cleavage events (TINCLEs, Lal et al. 1969) as illustrated in Fig. 3. TINTs are now favored over TINCLEs, because the latter introduce additional observational biases and may be anomalously stabilized (e.g., Barbarand et al. 2003), making their lengths unrepresentative of the thermal history. The orientations of these tracks relative to the crystallographic c-axis are also usually measured to account for differences in both etching and annealing characteristics of tracks in different orientations. Confined tracks show the closest approximation to the true lengths of unetched fission tracks, although their measurement is still subject to various unavoidable, but well-understood, sampling biases (Galbraith 2005).

Due to the limited accuracy of vertical movement in earlier-generation microscopes, measurements are usually made only for *horizontal* confined track lengths, thereby avoiding the need to correct for track inclination (Laslett et al. 1982). Modern microscopes have overcome this problem, so that it is now possible to accurately measure confined tracks of any orientation, which obviously increases the sampling size. Typically the lengths of around 100 confined track lengths are measured, although this may not be possible in samples with low track densities.

The number of TINTs in a particular sample can be enhanced by implanting artificial fission tracks from a ^{252}Cf source (Donelick and Miller 1991). This increases the number of etch channels to maximize the likelihood of TINT intersections below the surface and is especially useful where too few confined tracks can be found naturally.

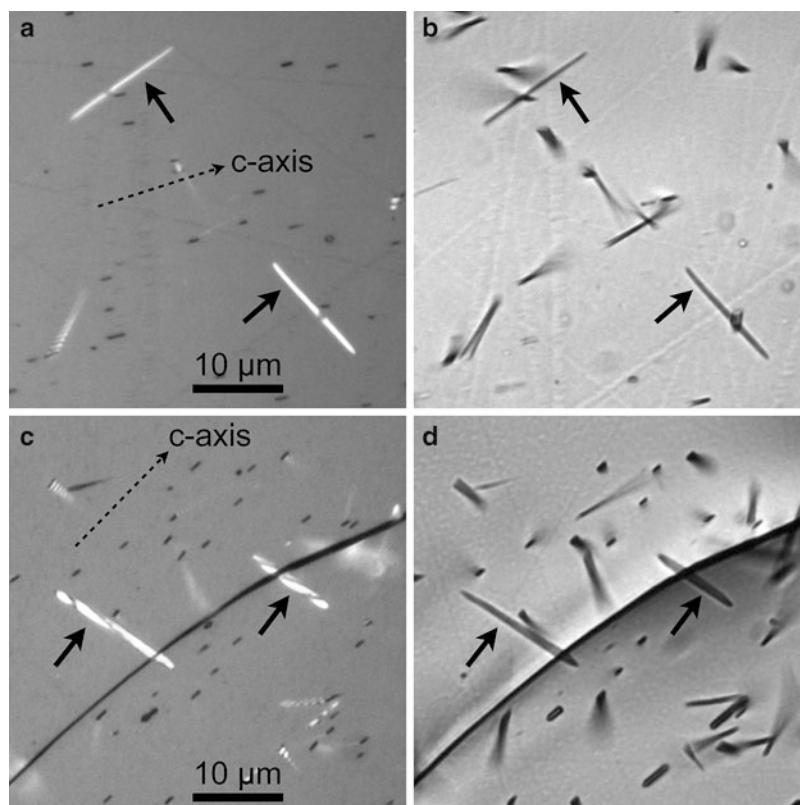


Fig. 3 Photomicrographs of confined fission tracks in apatite in reflected (*left*) and transmitted light (*right*). Two track-in-track (*TINT*) features are highlighted by arrows in (a) and (b), and two track-in-cleavage (*TINCLE*) features in (c) and (d). The dashed arrows show the crystallographic c-axis direction defined by the elongation of the surface track etch pits in reflected light

Track Diameter Measurements

Measurements of track diameters were first used in natural tektite glasses as a means for correcting the apparent fission track ages for partial loss, or fading, of the spontaneous tracks (e.g., Storzer and Wagner 1969; see “► [Impact Glass \(Fission Tracks\)](#)”). This followed the observation that etched diameters of spontaneous tracks were smaller than induced tracks, and experiments revealed a relationship between the reduction in track diameter and the track density. Although his approach worked well for glasses, a similar approach for minerals was much less successful as corrected ages rarely relate to the formation age of the host sample.

Fission track fading or annealing in apatites is influenced by their chemical composition (see section “[Experimental Fission Track Annealing Studies](#)”), primarily variations in chlorine concentration (Green et al. 1985). The rate of etching is also observed to vary with composition in apatite, such that the tracks appear more strongly etched in some cases than others after constant etching. Measuring track diameter parameters such as D_{par} and D_{per} – the average diameters of etch pits parallel and perpendicular to the crystallographic c-axis, respectively (Fig. 1) – can thus be used to indirectly monitor the annealing sensitivity of apatite (Donelick et al. 2005). D_{par} values typically vary between about 1.2 and 3.5 μm across the range of natural apatite samples. Although there is a coarse correlation between D_{par} and chlorine content of different apatites (Donelick et al. 2005), this relationship becomes less clear for the most common fluorine-rich varieties of apatite (e.g., Green et al. 2005) leading to some debate about the usefulness of D_{par} alone to monitor track annealing.

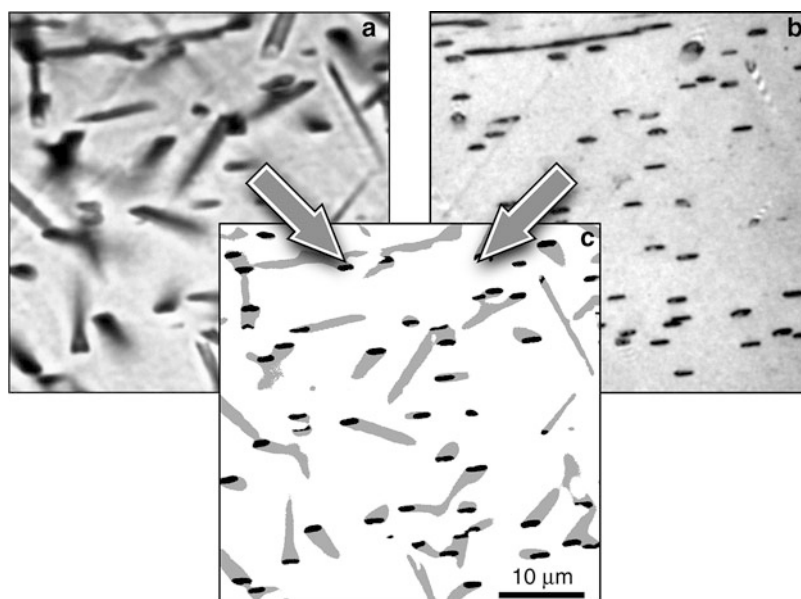


Fig. 4 Automated counting of fission tracks by *coincidence mapping*. The procedure digitally combines a slightly defocused transmitted light image (**a**) and a focused reflected light image (**b**) of the same tracks to obtain the overlapping features shown as black spots in (**c**), which are then analyzed automatically to obtain the number of tracks, discriminate track overlaps, and determine dimensions such as D_{par}

Automation of Fission Track Measurements

The latest generation of fully motorized digital research microscopes allows for comprehensive computer control of all aspects of microscopy and the acquisition of high-quality digital images. This new technology has converged with rapid increases in computing power and cheap availability of abundant digital image storage to bring new opportunities for automation to the laborious process of fission track data collection.

Gleadow et al. (2009) have described a procedure that makes use of these new technologies to implement autonomous digital imaging and automatic counting of fission tracks using image analysis. The emphasis has been on counting tracks in apatite and mica to support the great bulk of fission track analysis conducted today, but the system is readily adaptable to other minerals, glasses, and plastic track detectors. The central procedure of *coincidence mapping* relies on the digital comparison of pairs of reflected and transmitted light images for each microscopic field of view, as illustrated schematically in Fig. 4. A detailed Z-stack of transmitted light images is also captured at the same location to provide a fully focusable image of each grain for later inspection. The system also includes a comprehensive set of partially automated tools for locating suitably oriented grains in the mount as well as measuring various geometric parameters, including c-axis orientation, track length, and orientation, and D_{par} .

Methods of Dating

Fission Track Methods

As in any radiometric dating method, determining a fission track age involves obtaining a measure of both the parent isotope and the daughter products of the decay scheme. In this case, the number of decay events (daughter products) is measured using the spontaneous track density as described in

section “[Track Counting](#).” The parent isotope, ^{238}U , is normally estimated indirectly by using ^{235}U as a proxy, the concentration of which is obtained by counting the number of induced fission tracks produced during thermal neutron irradiation (see section “[Track Counting](#)”). Induced tracks are related to the ^{238}U concentration via the known $^{235}\text{U}/^{238}\text{U}$ ratio, which can be taken as constant (0.73 %) in natural geological materials, and the total neutron fluence received.

Most fission track dating techniques, therefore, require determination of the ratio of spontaneous to induced track densities in a sample and measurement of the neutron fluence received. There are a number of ways in which these variables can be determined (Gleadow 1981; Hurford and Green 1982; Wagner and Van den haute 1992; Gleadow et al. 2002). In *grain-population* methods, both spontaneous and induced track densities are determined as averages over a large number of mineral grains from different aliquots, while *grain-by-grain* methods allow individual ages to be determined for each analyzed mineral grain. Since the 1980s, just one of the grain-by-grain methods, the external detector method (EDM, see section “[The External Detector Method](#)”), has become standard practice for the great majority of mineral dating studies due to its analytical convenience and the individual grain data that are acquired.

An important recent development is the emergence of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) as routine tool for the precise analysis of trace elements in minerals. This method can measure the concentration of the parent isotope ^{238}U directly, rather than via ^{235}U , thereby eliminating the need for neutron irradiation while maintaining many of the benefits of the EDM method (see section “[The Laser Ablation ICP-MS Method](#)”).

The Fission Track Age Equation and Calibration

The fission track age equation is a specialized form of the general radiometric age equation that expresses the fission track age (t in years) in terms of the ratio of the spontaneous fission track density ($\rho_s \text{ cm}^{-2}$) to the induced track density ($\rho_i \text{ cm}^{-2}$) as follows (Fleischer and Price 1964; Naeser 1967):

$$t = \frac{1}{\lambda_D} \ln \left(1 + \frac{\lambda_D \phi \sigma I \rho_s}{\lambda_f \rho_i} \right) \quad (1)$$

where

- λ_D = total decay constant for ^{238}U ($1.55125 \times 10^{-10} \text{ year}^{-1}$)
- λ_f = spontaneous fission decay constant of ^{238}U ($8.46 \times 10^{-17} \text{ year}^{-1}$)
- I = isotopic ratio $^{235}\text{U}/^{238}\text{U}$ (7.2527×10^{-3})
- σ = thermal neutron cross section for ^{235}U ($580.2 \times 10^{-24} \text{ cm}^{-2}$)
- ϕ = thermal neutron fluence (n cm^{-2})

A calibration factor g must be introduced if the spontaneous and induced tracks are measured on surfaces with different track registration geometries (spherical or half-spherical; see section “[The External Detector Method](#)”) and detection efficiencies, as is the case in the external detector method.

For methods that require neutron dosimetry, the neutron fluence is calculated from the following:

$$\phi = B \rho_d \quad (2)$$

where ρ_d is the induced track density measured in a mica external detector that was in contact with a uranium-bearing standard glass in the same irradiation package. The constant B is calibrated by comparison with independent thermal neutron fluence dosimetry.

Substituting Eq. (2) into Eq. (1) gives the general working form of the fission track age equation expressed in terms of the three track densities:

$$t = \frac{1}{\lambda_D} \ln \left(1 + \lambda_D \zeta g \frac{\rho_s}{\rho_i} \rho_d \right) \quad (3)$$

where

$$\zeta = \frac{\sigma I B}{\lambda_f} \quad (4)$$

The aggregate constant ζ (zeta) is calibrated empirically against a set of age standards and was introduced to circumvent uncertainties in the spontaneous fission decay constant and the neutron dosimetry calibration (Hurford and Green 1983). Suitable age standards are minerals from rocks that have cooled rapidly, such as undisturbed volcanic rocks, and have been precisely dated by other methods, most commonly by Ar/Ar dating.

In the case where the ^{238}U concentration of a mineral grain is determined explicitly using the LA-ICP-MS method (section “[The Laser Ablation ICP-MS Method](#)”), Eq. (3) above is modified to

$$t = \frac{1}{\lambda_D} \ln \left(1 + \lambda_D \xi \frac{\rho_s}{C_U} \right) \quad (5)$$

where

$$\xi = \frac{A}{\lambda_f N_0 R \alpha} \quad (6)$$

and

C_U = concentration of ^{238}U

A = atomic weight of ^{238}U

N_0 = Avogadro’s number

D = density of the mineral

R = average etchable range of one fission fragment

α = detection efficiency for the etched surface

As for the zeta calibration approach described by Eq. (4) above, the aggregate constant ξ (Xi) in Eq. (6) can also be calibrated empirically against a set of age standards. However, all of the constituent constants are known, at least in principle, or can be determined explicitly, so that an absolute determination of the age is also possible.

The External Detector Method

In the external detector method (EDM), spontaneous tracks are measured on an internal surface in the etched mineral grains and induced tracks in an external track detector held firmly in contact with the mineral surface during irradiation. The external detector is almost always a cleaved surface of low-uranium muscovite. During neutron irradiation, some of the induced fission fragments from ^{235}U in the mineral grains leave the surface and enter the external detector. It is important to note that an external detector only receives tracks from one side (2π or hemispherical track registration

geometry), compared to the case of spontaneous tracks etched on an internal surface, which receives tracks from both sides (4π or spherical registration geometry).

After irradiation, the mica external detectors are etched to reveal patches of induced tracks corresponding to each grain in the mineral mount. As the grain mount is not etched again after irradiation, only spontaneous tracks are visible there, while only induced tracks are visible in the external detector. The etched surfaces have a mirror-image relationship to each other and are affixed side by side to a microscope slide for counting of exactly matching areas of spontaneous and induced tracks. Matching between grains and mica is usually automated using a computer-controlled stage.

An age determination by the EDM proceeds by selecting suitable grains in the mount, counting the spontaneous tracks present, and then counting induced tracks over the corresponding area on the external detector. Poorly orientated grains, those with nonuniform uranium distributions, or those with interference from dislocations or other defects, are simply avoided.

An important advantage of the EDM over alternative fission track methods is that data are collected over individual grains. Normally, about 20 grains are counted so that the resultant single-grain age distribution can be tested statistically to see whether they represent a uniform age population or not. Since the 1980s, the EDM has become the standard method for fission track analyses, being applied almost universally of studies of apatite, zircon, and titanite, as well as occasional analysis of other uranium-bearing minerals, such as garnet and epidote.

Neutron Dosimetry

For the external detector, and all other methods of fission track analysis that utilize neutron irradiation, it is vital to monitor the total neutron fluence received by each grain mount during irradiation in order to know how much of the ^{235}U has undergone fission during irradiation. This is accomplished by including neutron flux monitors in the same irradiation package as the prepared mounts. Flux monitors are positioned at the top and bottom of each package to monitor the total neutron fluence received and correct for any flux gradients. Once the neutron fluence is known for each sample in the irradiation package, uranium concentrations can be calculated for each analyzed mineral grain based on the corresponding number of induced tracks recorded in the external detector.

Typically these flux monitors are simply muscovite external detectors attached to pieces of reference glass with a well-known and homogeneous uranium concentration, allowing standard glass track densities to be determined in the etched external detector. Although flux monitors may be calibrated against the absolute thermal neutron fluence (Wagner and Van den haute 1992), the fluence calibration is usually included in the aggregate zeta constant (see section “[The Fission Track Age Equation and Calibration](#)”) so that the standard glass track density is applied directly in the age calculation (Eq. 3).

Neutron dosimetry-based methods have the advantage that they are all based on a ratio of two track density measurements, which have similar properties and are therefore likely to be subject to similar errors that ideally should cancel out. Significant disadvantages include very long sample turn-around times while the samples are away at the reactor and the necessity of handling radioactive materials after they are returned from irradiation.

The Laser Ablation ICP-MS Method

Over the last decade, the emergence of LA-ICP-MS to directly measure the ^{238}U concentration has the potential to rival, and even replace, the EDM (Hasebe et al. 2004). Sample preparation and etching proceeds in much the same way as for the EDM, and, as before, a series of well-oriented mineral grains are selected on an internal surface. Once the spontaneous tracks are counted, the

sample is placed into a laser ablation chamber, and an area of each counted grain is ablated and analyzed in the mass spectrometer.

As grains are typically small (~100 µm), a single laser spot with a diameter of 20–40 µm is usually used to ablate part of the mineral. An inert gas transports the aerosol from the ablation chamber into the plasma torch of an ICP-MS, where the ablated molecules are dissociated and ionized before being bled into a quadrupole mass spectrometer for analysis. The measured ^{238}U signal is then normalized using a stoichiometric isotope of known (or assumed) concentration such as Ca or Si to correct for variations in the ablation volume and the absolute concentration determined relative to a standard of known composition (see “► [Laser Ablation Inductively Coupled Plasma Mass Spectrometer \(LA-ICP-MS\)](#)”).

The LA-ICP-MS method can be applied to a range of different minerals and produces single-grain analytical data of comparable precision to the EDM. This new approach has the additional advantages of simplified sample preparation procedures, rapid and largely automated analysis, and needs only one (spontaneous) instead of three (spontaneous, induced, and standard glass) track densities. Most importantly, however, it does not require neutron irradiation and therefore eliminates the need to handle irradiated materials, resulting in dramatically reduced sample turn-around times. Although significant work still needs to be done on calibration, standardization, and testing, this technique is likely to be adopted much more widely in the near future.

One disadvantage of the LA-ICP-MS method is that it is a destructive technique on a microscopic scale, destroying part of each grain during analysis so that later inspection of the counting results is not possible. However, this shortcoming can easily be overcome if image sets are captured before ablation (see section “[Automation of Fission Track Measurements](#)”), thus creating a permanent digital record of each grain.

Fission Track Annealing and Modelling

It was discovered early in the development of fission track dating that fission tracks are stable over geological time only at relatively low, near-surface temperatures. As the temperature is raised, the radiation damage making up the core of each track is progressively repaired until the track no longer forms a continuous defect that can be revealed by etching. This process of fission track fading upon exposure to elevated temperatures is called *thermal annealing*, or often simply annealing.

Thermal annealing is a kinetic process in which temperature and time can to some extent be interchanged with each other, longer exposure to lower temperatures producing the same effect as shorter exposure to higher temperatures. Each mineral shows a different characteristic temperature range over which fission track annealing occurs, often referred to as the *partial annealing zone*. For apatite this annealing range is approximately 60–120 °C over geological heating times, with significantly higher characteristic annealing temperatures of around 150–200 °C for zircon and 200–250 °C for titanite, although these are not as well constrained as they are for apatite. A quantitative understanding of the track annealing process is critical to the use of fission track analysis for thermochronology.

Environmental parameters other than time and temperature (e.g., pressure, ionizing radiation) have no significant effect on fission track annealing (Fleischer et al. [1965b](#)), at least at the upper crustal pressures under which thermal annealing of fission track occurs in commonly used minerals such as apatite (Schmidt et al. [2014](#)).

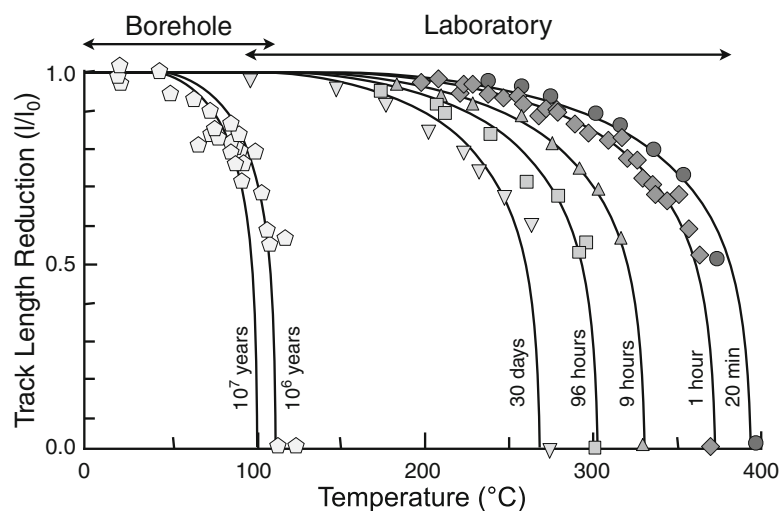


Fig. 5 Comparison of the effect of thermal annealing on fission tracks on laboratory (*right*) and geological time scales (*left*). Laboratory annealing data (from Green et al. 1986) show the reduction in mean confined track length (l) relative to the length of unannealed induced tracks in the same apatite (l_0) after heating at various temperatures and times. Similar length reduction is shown by spontaneous tracks in apatites from deep boreholes in the Otway Basin of SE Australia (from Gleadow and Duddy 1981)

Experimental Fission Track Annealing Studies

Thermal annealing of fission tracks in a particular mineral can be studied in the laboratory by observing the effects of different time and temperature treatments on freshly induced ^{235}U tracks on the assumption that these will behave identically to ^{238}U tracks. The degree of annealing is then monitored by measuring the length distribution of confined fission tracks.

The results of numerous such studies have led to quantitative models of fission track annealing in different minerals that may be extrapolated from laboratory to geological time scales (e.g., Laslett et al. 1987; Carlson et al. 1999; Barbarand et al. 2003 for apatite; Tagami et al. 1998 for zircon). Figure 5 shows the effects of laboratory annealing on induced track lengths in Durango apatite over different time scales (Green et al. 1986). The longer the exposure time, the lower the temperature required to produce a given degree of track shortening due to annealing. Extrapolations of the annealing curve for this apatite are also shown for heating times of 10^6 – 10^7 years using the annealing model of Laslett et al. (1987), along with observational data from deep borehole samples from the Otway Basin (Gleadow and Duddy 1981). The Otway apatites show a range of compositional variation, which broadens their annealing behavior compared to the single Durango apatite composition. However, the general consistency and similar form of the annealing curves between the borehole and laboratory results strongly suggests that annealing is being caused by the same mechanism in both cases.

In apatite, another important control of fission track annealing is the mineral composition. Apatites from most geological environments are dominated by fluorapatites, but also grade in composition toward chlorapatite, and, less commonly, hydroxyapatite. Fission tracks in more chlorine-rich apatites are more resistant to thermal annealing than those in fluorapatite as illustrated in Fig. 6. As described earlier (see section “Track Diameter Measurements”), etched track dimensions such as D_{par} also correlate to some degree with composition and may thus be used as a kinetic parameter to assess the annealing sensitivity of a particular apatite.

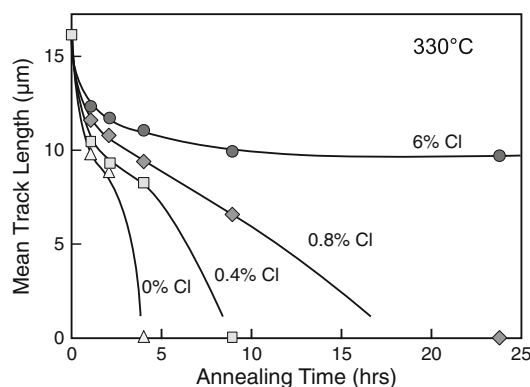


Fig. 6 The effect of chemical composition on experimental fission track annealing in apatites. The diagram shows the results of an isothermal annealing experiment where four apatites with different chlorine concentrations were annealed at the same temperature, 330 °C, for different times from 1 to 24 h. The higher the chlorine concentration of the apatite, the more resistant are the fission tracks to thermal annealing (Data from PF Green)

Thermal History Modelling

Track shortening during thermal annealing has two important consequences for fission track analysis. One is that each individual spontaneous track in a natural sample experiences a different fraction of the host rock's total thermal history and will shorten to a degree determined by the maximum temperature experienced since track formation. Because all of the tracks are of different ages, being added progressively by radioactive decay, a spectrum of track lengths results that contains a detailed record of the entire annealing history within the temperature range of the partial annealing zone. The second effect is that fewer tracks will intersect a given surface as the average track length gets shorter during annealing, so that the apparent fission track age is reduced proportionately during annealing. Thus, partial thermal annealing will have the effect both of reducing the fission track age and changing the track length distribution. Utilizing fission track analysis for thermochronology involves modelling the information in both the apparent ages and track lengths to reconstruct the thermal history, based on a quantitative understanding of the annealing kinetics from laboratory experiments (see section "[Experimental Fission Track Annealing Studies](#)").

Based on these annealing models, it is possible to *forward* model the distribution of fission track lengths and ages, whereby the two parameters are predicted for any given temperature-time path, and manually compared to the measured data. While this approach is useful to guide further interpretation, it is also relatively inefficient. In *inverse* modelling, a realistic thermal history is reconstructed from a given set of observed fission track measurements of age and length. Such inverse modelling is achieved by conducting numerous, random thermal history trials and testing the simulated forward models for their closeness of fit to the observed fission track parameters. Eventually after a very large number of trials, a number of good-fitting thermal histories emerge that match the observational data within defined statistical limits. However, it is important to note that such model solutions may not be unique, as different thermal histories can result in similar age and track length distributions.

Thermal histories can be further constrained by adding independent geological information (e.g., geochronological data, depositional age, etc.) or by modelling fission track data in conjunction with other thermochronometers such as (U/Th)–He or vitrinite reflectance. Efforts are also being undertaken to allow more sophisticated modelling of samples within their geological context, for example, by modelling a series of neighboring samples simultaneously or by integrating thermal history

modelling with structural or geological models. The strategies for inverse modelling of fission track data for reconstructing thermal histories are discussed in detail by Gallagher (1995, 2012) and Ketcham (2005).

Summary and Conclusions

Fission track dating has been applied to a wide diversity of geological and occasionally archaeological problems, with an early emphasis on dating such exotic materials as meteorite impact glasses and volcanic glasses associated with important hominin fossil sites. These early studies have largely been replaced by a much larger body of work on accessory minerals, such as apatite and zircon, from common crystalline rocks. In this later phase, fission track analysis has developed as one of the core methodologies of thermochronology, and applications to stratigraphic dating have largely given way to other techniques.

The progressive development of a quantitative understanding of fission track annealing under elevated temperatures has led to the major application of fission track dating today in thermochronology, particularly centered on apatite, which is by far the best understood and most commonly used mineral system. Fission track thermochronology has been widely applied to studies of tectonic and exhumation processes in both convergent and extensional settings (see “► [Tectonic Processes \(Thermochronology\)](#)”; “► [Exhumation \(Thermochronology\)](#)”), fault movements (see “► [Fault Zone \(Thermochronology\)](#)”), sedimentary basin analysis, provenance studies (see “► [Provenance \(Thermochronology\)](#)”), and landscape evolution (see “► [Thermochronology, Landform Evolution](#)”). Various applications of fission track dating have been reviewed in Wagner and Van den haute (1992), Gallagher et al. (1998), Gleadow et al. (2002), and Reiners and Ehlers (2005).

Rapid advancements are still taking place in fission track techniques, and in particular, the emergence of new methods involving laser ablation ICP mass spectrometry and automated image analysis are likely to lead to a further transformation of fission track thermochronology in the coming years.

Cross-References

- [Apatite](#)
- [Ar–Ar and K–Ar Dating](#)
- [Exhumation \(Thermochronology\)](#)
- [Fault Zone \(Thermochronology\)](#)
- [Hominid Evolution Timescale](#)
- [Impact Glass \(Fission Tracks\)](#)
- [Laser Ablation Inductively Coupled Plasma Mass Spectrometer \(LA-ICP-MS\)](#)
- [Provenance \(Thermochronology\)](#)
- [Radiation Defect](#)
- [Tectonic Processes \(Thermochronology\)](#)
- [Tektites](#)
- [Thermochronology, Detrital Zircon](#)
- [Thermochronology, Landform Evolution](#)
- [U-Series Dating](#)
- [Uranium-Lead Dating](#)

- [U–Th:He Dating](#)
- [Volcanic Glass \(Fission Tracks\)](#)
- [Zircon](#)

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Electron Spin Resonance (ESR) Dating, General Principles

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Synonyms

[Electron paramagnetic resonance \(EPR\)](#)

Definitions

Electron spin resonance: The identification of paramagnetic species through absorption of energy in an external magnetic field.

Electron spin resonance dating: The determination of burial age through measurement of the concentration of free radicals created by natural radiation.

Introduction

To understand electron resonance (ESR) dating, one must, clearly, first understand the principles of electron spin resonance spectroscopy. As the name shows, these principles begin with the nature of atomic structure – a positively charged nucleus surrounded by negatively charged electrons. The technique of ESR spectroscopy was first developed by Zavoisky in 1944. Since then applications have been developed in multiple fields of chemistry and physics, as well as the potential for dating in geology, paleontology, and archaeology. An excellent summary can be found in Rink (1997).

Quantum theory tells us that all systems have a definite energy. Every spectroscopic method involves transitions between two states due to input of energy to a material. If the energy provided to the system exactly matches the difference between two states (resonance), the system can be moved from one state to a higher one, and this yields an absorption signal. Transitions from higher to lower levels also occur, and the emitted energy again provides a measure of the difference in energy between levels. Common techniques in chemistry and physics, defined by the relevant range of the electromagnetic spectrum, are optical spectroscopy, infrared (IR) spectroscopy, and ultraviolet (UV) spectroscopy. ESR spectroscopy almost always involves absorption of energy in the microwave region.

For atoms and molecules, these states can be defined by a series of quantum numbers that are related to angular momentum. ESR spectroscopy, as the name suggests, is concerned with transitions of electrons between states of differing electron spin. As a spinning electric charge, electrons possess a magnetic moment. The interaction of this moment with an applied external magnetic field leads to Zeeman splitting of possible states as shown in Eq. (1), where β is the electron Bohr magneton, H is the applied field, g is the splitting factor for a given system, and M_s is the electron spin quantum number:

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$$\Delta E = g\beta H M_s \quad (1)$$

For a “free” electron, the simplest case, $g = 2.00232$, and we consider only the two possible spin states $M = \pm 1/2$. The associated magnetic moments are equal and opposite in direction. Figure 1 shows the effect of applied magnetic field on the separation between the possible states. The lower state represents a system in which the magnetic moment of the electron is aligned parallel to the external field, while in the upper state they are opposed. Quantum mechanical calculations can determine the energy of a given state. Fortunately, quantitative knowledge of absolute energies is not needed in order to use this technique for dating.

Now we need to remember another chemical principle. Electrons are normally paired, either in atomic orbitals or in chemical bonds. By the Pauli principle, the spins of the paired electrons must be opposite in direction. If, then, such a material is put in a magnetic field, each state will be populated by one electron. If we put in energy to raise the lower electron to the upper state, we have reversed its spin and we now have a forbidden situation, a level with two electrons of the same spin. Thus electron spin resonance can only be observed in systems with unpaired electrons. Such systems are called “paramagnetic,” and an alternate name for the method is electron paramagnetic resonance (EPR). Which term is used is a matter of preference; physicists are more likely to use EPR. The principles are the same; the only problem that this introduces is the need to search under two names to obtain all the available references in the field.

Those readers with experience in optical, IR, or UV spectroscopy will be accustomed to scanning by changing wavelength. The atomic or molecular orbitals have fixed energies. ESR spectrometers scan by changing the magnetic field. Figure 1 shows that the splitting between levels is a function of magnetic field. So we change H until the splitting matches a constant energy, $h\nu$. In theory we could hold H constant instead, but experiment has shown that we get better precision the other way.

There is a second difference between other methods and ESR spectra. In other methods, the resonance signal is indicated by an absorption (or transmission) peak such as that in Fig. 2. Largely because of details of signal acquisition by the spectrometer, ESR spectra are collected as the first derivative of the peak. This has one significant advantage for chemists and physicists. Frequently their interest is in the dependence of the g -value on electronic environment. Using the derivative spectrum, one can more easily see small changes in g -values by measuring the change in position of the point where the signal crosses the baseline rather than by attempting to find the maximum of the peak itself.

Figure 2, of course, shows only the simplest spectrum, isotropic absorption by a free electron. Few ESR spectra match this simplicity. Multiple unpaired electrons, such as those on manganese, result in a spectrum of multiple lines with equal intensities (fine structure). In many cases, g -values are

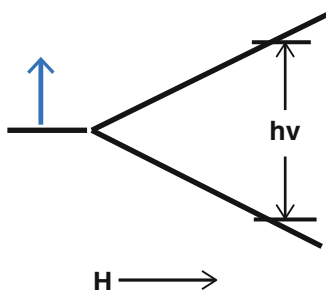


Fig. 1 Effect of Zeeman splitting on electron energy. As the magnetic field strength (H) increases, the energy difference between the spin states increases. The unpaired electron (*blue arrow*) will move from the lower level to the upper if an amount of energy, $h\nu$, is added to the system

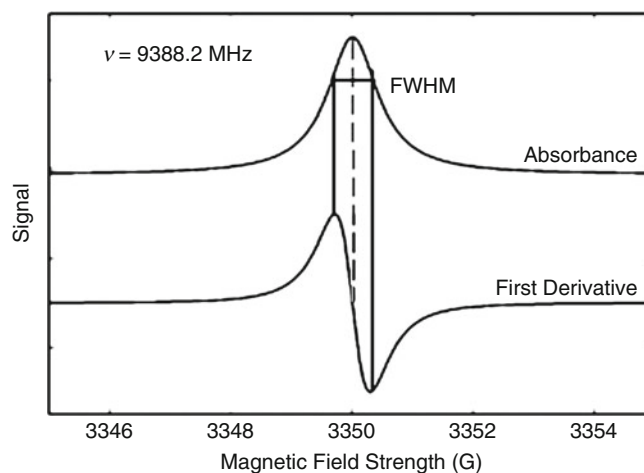


Fig. 2 Relationship of absorbance to first derivative spectrum as seen in ESR spectroscopy

Table 1 Comparison of ESR spectrometric bands. ν , microwave frequency; H_0 , field strength

Band	ν (GHz)	H_0 (mT)
L	1.5	53.5
S	3.2	114
X	9.5	339
K	25	892
Q	35	1,250

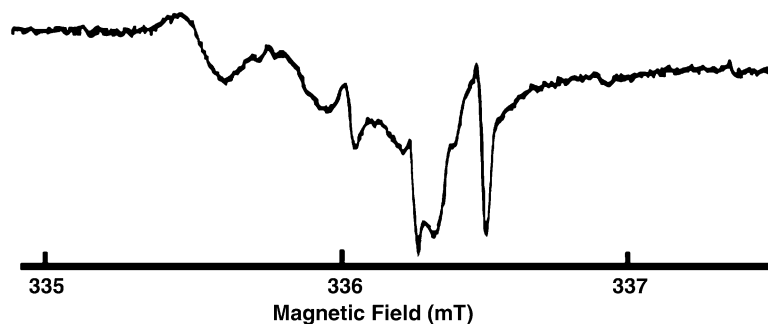


Fig. 3 Spectrum of natural flint with complex peaks

affected by interactions with nuclear spins (hyperfine splitting), and for solid materials, such as those normally used for ESR dating, by variable orientations of crystals with the magnetic field (Ikeya 1993). These, with symbols such as $g_{\perp}$ and $g_{\parallel}$, will be mentioned under specific applications.

Fortunately most of the dating applications can ignore this complication. For a given substance, dating specialists have established the optimum line to measure, whether it be the complex spectrum of aluminum or the anisotropic carbonate spectrum. More problematic is the mixture of elements found in most natural materials. This can yield a complex spectrum of overlapping lines from which the desired information must be extracted by suitable adjustment of experimental parameters,

including temperature of measurement. Figure 3, a spectrum of raw flint, is an example where the spectrum contains contributions from the E' silica peak, a peroxy peak, and organics (plus some others).

Complex spectra can sometimes be resolved by increasing the resolution, separating overlapping signals. The more intense the magnetic field, the easier one can resolve two signals whose g-values are virtually identical. ESR spectrometers are defined by the frequency of the microwave source (see Table 1). The most commonly used type is X-band, but higher bands, especially K and Q, also have a role in ESR dating. There is, however, a trade-off. The higher the band, the smaller the amount of sample used, so that while the precision of the spectrum, in terms of separating signals with very similar g-values, is improved, the quantitation of the signal diminishes. The most useful dating application of Q-band spectroscopy is determining whether signals are related to the same radical species, and therefore, the less-well separated peaks in the X-band can be treated as a single signal (Skinner et al. 2001b).

ESR-Active Materials

So where do we find paramagnetic systems? There are three major classes. “Point defects” are electrons trapped during the formation of certain crystals. They are often responsible for colors. Some atoms, mostly transition metals, have an uneven number of electrons and therefore show paramagnetism. Iron is, of course, a well-known example here. Finally there are molecules which can develop paramagnetism in two ways. First, the molecular structure can be paramagnetic, usually because it incorporates one or more paramagnetic atom. Heme proteins, which contain iron, exhibit an ESR spectrum. Second, a molecule can be made paramagnetic by removing an electron from a molecular orbital. These are called “free radicals.” This class of materials is the one we look to for dating applications.

The free radicals with which we are concerned are created by radiation. There are three forms of nuclear radiation. Alpha (α) radiation is caused by emission of a helium nucleus from the radioactive atom. As this is a large particle, it is easily stopped with an effective range of approximately 20 μm . Beta (β) radiation consists of nuclear electrons. The energy of these particles can vary considerably; in materials common in dating, they are assumed to penetrate about 2 mm. Finally, gamma (γ) radiation is simply energetic photons that, again for this application, penetrate approximately 30 cm. Additionally, radicals can be induced by cosmic radiation, high energy particles with extensive penetration capability (Prescott and Hutton 1988).

Nuclear radiation, whether alpha, beta, or gamma, can break chemical bonds to form radicals; it can also remove an electron from an atom or molecule. One interesting result is the production of the point defects mentioned earlier. Irradiation of colorless gems has been used to simulate rarer colored versions, often without mentioning the artificial transformation (e.g., Steinhäuser et al. 2013). Common radicals in current scientific discussion are those in the atmosphere that result in the “ozone hole.” Low-level natural radioactivity in the environment is continually “damaging” materials. Living systems have mechanisms to repair this damage at these low levels, but once the system has died, radicals begin to accumulate. Not all radicals can be used for dating, however.

Before delving deeper into ESR, one might note that there are other dating methods based on the creation of trapped charge by radiation. Usually electrons are trapped at radiation defects in this process. Collectively they are called “trapped charge” methods. The oldest of these is thermoluminescence (TL), where the accumulated damage is detected by heating the sample and measuring the energy released as the electrons are released from trapped charge sites and migrate to luminescence

centers. Optically stimulated luminescence (OSL) uses photon excitation to release the energy (Aitken et al. 1993).

Geological, Paleontological, and Archaeological Dating

General Considerations

A good dating method requires three things. Firstly the dating signal must be zero, or must be determinable, at the time of the event being dated. Secondly, the signal must change in a predictable and consistent manner with time. Thirdly, the signal must be stable over the time period in question. Paramagnetic systems can be annealed (revert to diamagnetic, or paired electrons) in several ways. A paramagnetic molecule may react with another, taking an electron from the second one. The second one may then become paramagnetic but the first has lost this property. Paramagnetic systems tend to be unstable and anneal spontaneously with time (more on this later). This process can be accelerated by heat.

As examples of the first factor, consider flint artifacts. For most of human history, these were made by flaking natural cobbles. While flint has an ESR signal, the signal we would see would be that accumulated since the flint was formed, not since the artifact was created. Hence we only date flint that was heated in the process of manufacturing an artifact. On the other hand, biological materials such as shell, coral, and teeth do not have a “native” signal that prevents dating. This has been investigated by studying modern examples.

The change in signal intensity with time depends on two factors. The first is the sensitivity of the material to radiation and is relatively easy to discover. Initially a linear dependence on dose was assumed, but that was soon shown to be incorrect (Skinner 1983). For most of the last 30 years, the growth curve shape has been assumed to be a saturating exponential. While this is still largely the case, other dependencies have also been determined. For the aluminum center, for example, it appears that there are two components, and a linear term has been added to the exponential. In other cases, two exponential terms have been suggested (Haskell et al. 1997; Duval 2012). Improvements in instrumental precision are likely to continue to improve our understanding of dose dependence.

The other factor is the dose rate, the amount of radiation delivered per unit time. Dose rates are found by summing α , β , γ , and cosmic contributions. Unfortunately, the dose rate may change with time. Unlike radiocarbon ages, ESR ages depend on the environment of the sample, and that may vary during burial. A cave deposit is perhaps the most stable, but even then the moisture content within the cave may not be constant. A sample taken from a riverbank may not be in its original deposit, so the modern environment we measure to establish an age may not reflect the actual burial history. At present, environmental variability is the greatest source of uncertainty in ESR dating, made worse by an inability to quantify it with a level of precision comparable to that we can achieve in the laboratory when we are measuring ESR spectra. This will be covered in more detail later in this section.

In comparison, determining signal stability is relatively straightforward. Recall that unstable systems, such as our paramagnetic radicals, can be annealed with heat. The degree of heat required, measured both as time of heating and temperature, depends on the stability. For background, consider the kinetics of a reaction. For every reaction there exists a rate law defining the change in concentration of reactant (or product) with time. For the annealing of radicals, that law is very simple. In integrated form,

$$C - C_0 = -kt \quad (2a)$$

where C is the concentration of radicals at time t , C_0 is the radical concentration at $t = 0$, and k is the rate constant which depends on temperature. Conventionally, one measures the signal intensity (proportional to concentration of radicals) as a function of heating time for a fixed temperature. From that one can calculate the half-life (mean lifetime) at that temperature, the time needed to reduce the signal to half its original value, and from that the rate constant, k :

$$0.5C_0 - C_0 = -kt_{1/2}, \quad \text{or} \quad k = 0.5C_0/t_{1/2} \quad (2b)$$

In 1889, the Swedish chemist Svante Arrhenius derived a relationship between temperature and reactivity. Arrhenius' law can conveniently be written as

$$\ln k = \ln A - (E/RT) \quad (3)$$

where E is the energy needed to restore the system to stability, A and R are constants, k is the rate constant, and T is temperature in degrees Kelvin. To use this equation, one measures k at a series of temperatures well above the environment, usually around 100–300 °C, in order to speed the reaction. One then plots $\ln k$ against $(1/T)$. Extrapolating this plot to ambient temperature provides the mean lifetime at this temperature. The extrapolation is usually quite imprecise, but it provides at least the order of magnitude of the mean lifetime in the external environment. The results also depend on the assumption that A remains constant over the temperature range between measured and ambient, but this holds well for this system. Other complications include changes in the ESR spectrum with temperature. Shells and teeth, for example, char at elevated temperatures and the resulting carbon radical can obscure the dating signal (Skinner et al. 2000).

ESR Spectra

With these general principles in mind, let us turn to the details involved in determining the age of a material that has a suitable signal and reasonable signal stability. For ESR dating the mean life of the signal should be an order of magnitude greater than the age being determined (Grün 2007). In theory, what we wish to know is the number of radicals produced as a function of radiation. For this we would normally look to the area underneath the absorption signal. As noted, ESR spectrometers produce the derivative of the signal. It is possible to integrate the signal, but instead we use the properties of the original curve. There is a mathematical relationship between the area under the peak and the full width at half maximum (FWHM). And as can be seen from Fig. 2, FWHM corresponds to the height of the derivative. Thus we can plot the peak height from the signal against radiation dose and obtain a proxy for area. This is only really true for well-shaped lines that are not influenced by other ones. As will be seen in later sections, this is almost never true, but again we can find approximations that are sufficiently close to the actual values that our results are reliable.

As noted earlier, crystalline symmetry affects the g -value. If the radical rotates freely within the crystal, the asymmetry averages out. If not, one can define a series of lines as, for example, $g_{\perp}$ or $g_{\parallel}$. The first and still best-known ESR dating signal is that of a carbonate-derived radical, and as commented briefly earlier, this has an anisotropic component. Experiments with ^{13}C -doped calcite [Callens et al. 1989] suggest that a signal at $g = 1.9973$ arises from hindered rotation of an orthorhombic CO_2 radical. The larger signal at $g = 2.0007$ has a contribution from the hindered rotating species, but also arises from a freely rotating radical. Both signals grow with radiation, so in principle either can be used.

Experimental parameters can be used to accentuate one signal over another in a complex spectrum. The intensity of a signal would be expected to grow with microwave power, and it does so up to a point. For every signal with which we will be concerned, there is a saturation power, above which the signal not only does not grow, but may actually decrease. The explanation for this is reasonably straightforward. In any spectroscopic system, not just ESR, there is a distribution of populations among energy states. For ESR, we need fewer electrons in the higher energy state than in the lower, since otherwise the electron in the lower state, even if excited by the resonant energy, has no place to go. Transitions are constantly occurring between states. The transition from the higher energy spin state to the lower is called the “relaxation time.” As long as the relaxation time is short, electrons will return to the lower state by thermal transfer to the crystal lattice fast enough to leave room for new electrons to be promoted to the higher state by microwave energy. For any new system, the signal intensity must be measured as a function of microwave power. While measurements of a specific line must be taken at powers below saturation, sometimes it is convenient to use saturation to simplify the spectrum. For example, by using powers >5 mW, the E' signal in silica can be suppressed (and conversely, if that line is to be measured, the power must generally be <0.1 mW) (Ikeya 1993).

Another experimental parameter is the modulation amplitude (also called modulation field width). To sharpen the output of the detector, the output current is modulated by a pair of coils mounted on the cavity (see Section C for details). Roughly speaking, this modulation amounts to sampling the output at a given interval, large if a large modulation amplitude, small if not. The larger the modulation amplitude (i.e., the larger the output sampled), the larger the resulting signal. If, however, the signal is complex, then a large modulation amplitude may distort the peak shape, mixing two signals. Some experimenters have deliberately overmodulated the signal, assuming that the mixed signals arise from the same radical and have the same half-lives (Molodkov 1998). Generally this is not true, and this technique is regarded with suspicion by most dating specialists.

How then does one set the spectroscopic parameters? Here we need to rely on experiment. If, using a given set of parameters, the peak heights obtained yield ages that are consistent within experimental error with other methods over a wide time range, then those parameters are the ones to use. This is the test that matters. Whatever “error” is introduced by assuming a Gaussian or Lorentzian line shape for a signal that is clearly neither must be much lower than the error introduced by other factors such as the dose rate discussed in the following section.

Dating Procedure

So to begin a dating experiment, select your sample. Generally the sample is powdered in order to ensure that the signal is independent of orientation within the cavity, and the powder is divided into multiple aliquots. If avoiding this sample destruction is essential, a solid piece can be used, but then one should take measurements at a variety of orientations. Either way, the first measurement is, of course, the spectrum of the native material. Then one takes either aliquots of the powder or the single solid piece and applies known artificial radiation doses. Now plotting the peak height against dose creates a “growth curve.”

The example in Fig. 4 assumes a simple saturating exponential growth. As noted earlier, various groups have found that other ways are appropriate to express the dependence of signal on dose in different materials, including double exponentials (Haskell, et al. 1997) and exponentials with a linear component (Duval 2012).

Extrapolating the growth curve (whatever the function used) to the x-axis gives the accumulated dose, the amount of radiation that the material experienced since formation, or burial. This quantity is variously known as AD (for accumulated dose, or occasionally archaeological dose) or ED

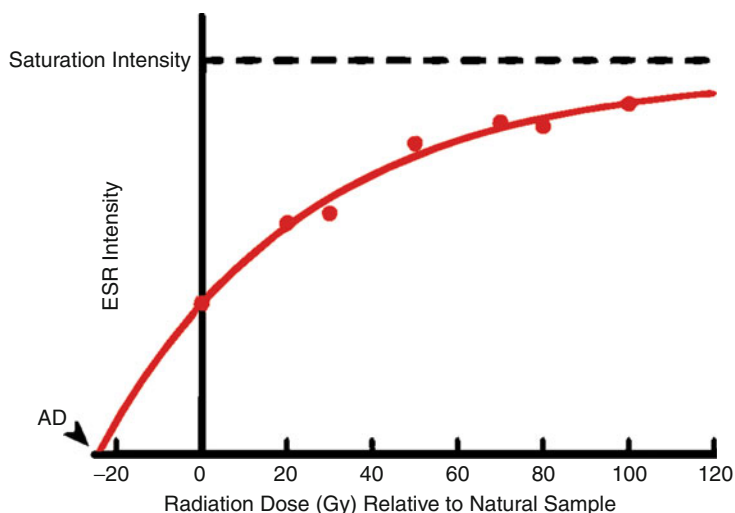


Fig. 4 Example of a growth curve in the form of a saturating exponential

(equivalent dose or environmental dose) or D_e (as before). Careful measurement and using a statistically significant number of points usually means that the error on AD is small.

Converting this information to a sample age can be complex. In the broad sense, the AD is the sum of dose rates times the time that has passed. Mathematically this can be expressed as

$$D_e = \int_a^r D(t) dt \quad (4)$$

As a practical matter, this requires knowing the sample environment. Recall that the contributors to environmental dose include α -, β -, and γ -radiation from radioisotopes inside the sample and in the sediment surrounding it, plus cosmic radiation. As a first approximation, we can express this as

$$AD = AD_{\text{ext}} + AD_{\text{int}} = D_{\text{ext}}t + D_{\text{int}}t \quad (5)$$

Consider first D_{ext} , the external dose rate. γ -radiation can penetrate 30 cm, so essentially one needs to know the complete environment in a sphere of 30 cm radius around the sample. In most cases one cannot determine this absolutely precisely. For one thing, the “top” half of the sphere has probably been removed in the course of excavation. More detrimental, the sediment at most sites is inhomogeneous, the so-called lumpy site.

Several methods have been used to obtain dose rate information. None of them are free of flaws. In situ gamma spectroscopy at the position of the sample can provide both the immediate gamma dose, including the cosmic component, and concentrations of the major radioisotopes from which β doses can be calculated. One difficulty is that this provides only an estimate on the remnant sediment, which may or may not be identical to that removed. Further, calibration of these spectrometers has been a problem (Lyons 1989; for a more recent view see Duval and Arnold 2013).

In a second method, dosimeters are inserted into the site, which measure the cumulative external dose, again the γ plus cosmic contributions. These are based on one of the other trapped charge methods, either TL or OSL. Both types have their proponents and detractors (McKeever and Moscovitch 2003; Richter et al. 2010). Either type of dosimeter must be left in place. Depending on the site, they could be retrieved after as short a time as a week or must remain for 6 months to a year. Thus placing a dosimeter at the precise sample location, needed for accuracy, in most sites

would imply suspending excavation in that area, hardly desirable. As a result, usually these are put in the walls, or other areas where they do not interfere with continued excavation. They therefore may not measure the local dose rate.

Another alternative samples a number of sedimentary units in the site and does a volumetric average of the dose rate from each. This may be needed for sites where a gamma spectrometer is not available, or the cost or complexity of retrieving dosimeters is a problem. However, both collection of a statistically significant number of samples and calculation of the resulting average are complex procedures. In principle, in calculating the volumetric average, one should consider, for example, exactly where every rock or bone is in relation to the sample.

If sedimentary analysis is chosen, there are again different ways of obtaining the analytical information. Gamma spectroscopy can be used for direct measurement of sedimentary radioisotope content in the lab. Another method commonly used is neutron activation analysis (NAA) of sediments. In NAA, samples taken from the site are bombarded with neutrons to stimulate nuclear reactions. Those associated with such elements as uranium, potassium, and thorium, the three most common contributors to environmental dose, give off energy of specific wavelength, with intensity proportional to concentration. The weaknesses in laboratory measurements are first that there may be other isotopes that are not captured, second that the actual intensity of radiation can be attenuated by water and thus the sediment moisture content has to be measured, and third that converting the concentration of, say, uranium to a dose requires assumptions about the chain of daughter products (Murray et al. 1992; Grün 1992). In particular, one has to make an assumption about whether radon has been captured in the sediment and therefore contributed to the dose or whether, as a gas, it has escaped. In addition, one has to estimate the contribution of cosmic radiation.

The approximations do not invalidate the results. When two methods such as TL dosimetry and sedimentology have been used on the same site, they yield similar ages for archaeological materials (Dibble et al. 2012), despite being based on different assumptions.

In comparison one would think that finding the internal dose rate, D_{int} , would be straightforward. For some materials it is. Unfortunately, most of the important materials for ESR dating are more or less porous. We can determine, again, the current level of radioisotopes in, say, a tooth, but from experience we know that this level has accumulated over time, perhaps quickly, immediately after burial, or perhaps slowly and continuously. Determining this uptake is a significant complication,

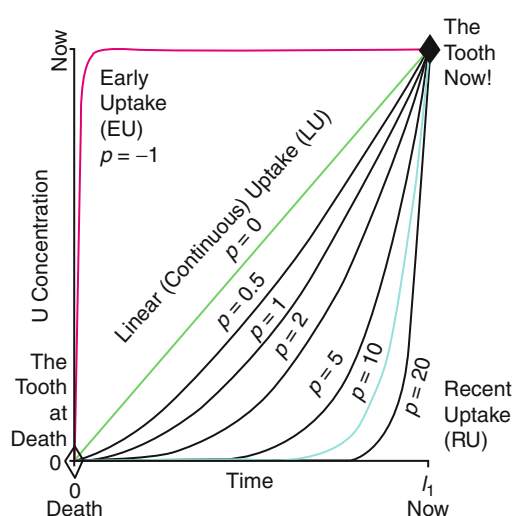


Fig. 5 Different possible uranium uptake models are defined by the parameter “p” (Figure courtesy of Dr. Bonnie Blackwell)

most notably for teeth but also for shells. Historically one modeled three possible types of uptake: early uptake (EU), in which uptake of uranium was essentially instantaneous; linear uptake (LU), in which the rate of uptake is constant over time; and recent uptake (RU), in which virtually all the uranium is absorbed by the sample in a short period before the sample is recovered. Figure 5 represents these options, using a parameter, p , to define them. Which option is most plausible depends on the sample environment. A constant environment is, naturally, likely to produce an LU age. A sample that is initially buried in a lake that then dries up may well fit the EU model. RU models can occur in two ways. The environment may change suddenly to one with more available uranium, perhaps due to tectonic activity. Or the sample itself may change. There is evidence that by 1 Ma, tooth enamel may develop microcracks, allowing more rapid absorption of uranium (Skinner et al. 2001b). And, of course, intermediate values of p are always possible (Blackwell et al. 2002). Recently a number of researchers have developed a coupled ESR/U Series method for teeth that can determine the time-averaged value of p and thus eliminate much of the uncertainty in uptake (Grün and McDermott 1994).

Determining the true uncertainty in the ESR age is difficult. Of course we know the uncertainty in measurements of, e.g., ED and the modern concentrations of radioisotopes, but we cannot know with the same certainty the history of the site. No matter what method is used to determine D_{ext} , it does not capture the overall variation in moisture, nor possible changes in overburden with accompanying change in cosmic dose. Even radon escape may vary with time. And we cannot quantify what we do not know. Two approaches can increase confidence in the results. One is the “isochron” method for tooth enamel that relies on multiple subsamples from a single tooth (Blackwell et al. 2001). More generally, we can recalculate the age as we vary factors such as average water content or cosmic dose rate (Deely et al. 2011). A simplified example is shown in Fig. 5 where dose rates from approximately 250–600 $\mu\text{Gy}/\text{year}$ still yield ages within the errors on the factors we can quantify. This exceeds variability found in virtually all sites (Fig. 6).

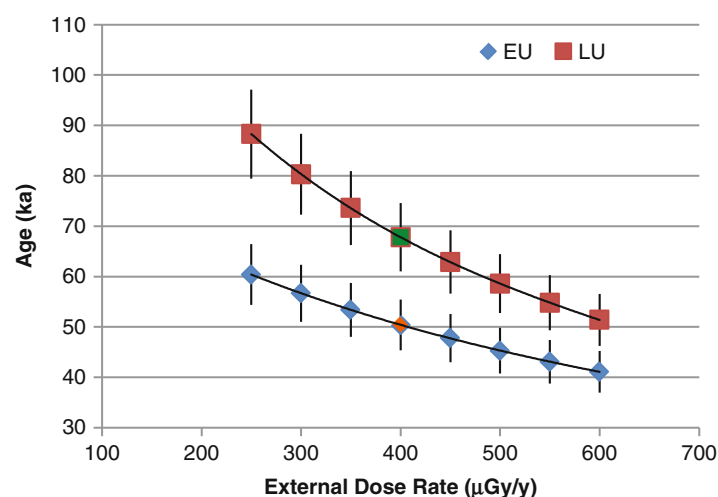


Fig. 6 Dependence of calculated age on external dose rate. As measured, the external dose rate for this sample was 400 $\mu\text{Gy}/\text{year}$. Error bars show 1 σ ; within 2 σ , ages are consistent for a given model over a range of dose rates from about 250 to 600 $\mu\text{Gy}/\text{year}$

Materials Used in ESR Dating

Carbonate

The most successful examples of ESR dating have involved carbonate-containing compounds. The major sample type, mollusks, deserves its own section and will not be discussed further. It is worth commenting, however, on speleothems, which were the first samples dated (Ikeya 1978). “Speleothem” is a general term for a variety of cave deposits resulting from dissolution and reprecipitation in limestone rocks. The general features of speleothem spectra resemble those of some mollusks. The primary difficulty in using them is contamination by inorganic and organic detritus which can lead to interfering peaks in the spectrum and misleading internal dose rates. An interlaboratory cross-calibration (Hennig et al. 1982) showed considerable inconsistencies, including disagreement as to the appropriate signal. Lyons (1989) undertook a systematic study of possible causes. There continue to be a number of studies (Bahain et al. 2011), but also suggestions that ESR is of limited utility for dating speleothems (Döppes et al. 2008).

A number of early studies of continental uplift used ESR dating of coral (Schellmann and Radtke 2004; Skinner 1985). Large coral reefs can serve as both the sample material and the surrounding “sediment.” Although the signal stability in coral should restrict its use to <500 ka, good agreement between ESR and other methods on coral has been found up to about 650 ka without correction for fading (Radtke et al. 1988). This suggests a large uncertainty in mean lifetimes determined by isothermal annealing. U-uptake may also be an issue here.

Other carbonate-containing materials have been considered for dating. Caliche and travertine have contamination problems. Foraminifera from deep-sea cores have been studied, with some success, but more work is needed (Schellmann et al. 2008).

Phosphates

The most useful substance for ESR dating has been tooth enamel. Hydroxyapatite (HAP), the structural mineral in teeth, is a phosphate. However, the ESR signal arises from carbonate inclusions in the HAP crystal, and hence the parameters for measuring are the same as for carbonates. The stability of the signal in enamel has been shown to exceed 10^{15} y (Schwarcz 1985; Skinner et al. 2000), allowing dating from as young as 30 ka to 3–4 Ma. Both ends of this range have been cross-checked with radiometric methods, ^{14}C for the younger samples (e. g., Rink et al. 1996) and Ar/Ar at Olduvai Gorge for the older (Skinner et al. 2001a).

Bone contains the same hydroxyapatite (HAP) as teeth and presumably the same carbonate impurities. Therefore, it would seem that bones could be used for dating. Two factors mitigate against this. The success of dating enamel is in part due to the signal stability attributable to large HAP crystals. Crystal size in bone is considerably smaller. More importantly, bone is quite porous. Uranium can be absorbed more easily, but also leached from bone during burial. This largely prevents precise determination of an internal dose. Early studies (Mascarenhas et al. 1982; Kai et al. 1988) seemed to show that ages could be measured within an order of magnitude and were more reliable for young bones, presumably because there was less time for absorption/leaching episodes. Currently, however, ESR dates on bone should not be considered dependable (Döppes, et al. 2008).

Silicates

Quartz grains in sediment were initially studied using the E' signal measureable at room temperature (e.g., Xu and Zhou 2009). A recent development has been the measurement in liquid nitrogen (LN₂) of optically bleachable signals in quartz sediment building on pioneering experiments by Toyoda

et al. (2000) and others. There are three of them, one deriving from aluminum centers, one from a Ti-H center, and one from Ti-Li. If ages determined for the three centers agree, then one has confidence in the results. These applications will be covered in more detail in a later section.

Quartz, in microcrystalline form, also exists as flint or chert. The presence of flint in many archaeological sites encouraged the dating community to look to all possible dating methods. Unfortunately, since trapped charge methods record all radiation since formation, ESR dating of unheated flint would at best date the creation of the raw material, not its conversion into a tool. The “skinflint” method hoped to get around this by comparing the damage to the outermost layer with that of the core, on the hypothesis that β -radiation from the sediment, present only after knapping, would penetrate the first 2 mm of the sample and provide a contrast to the overall dose (Schwarcz and Rink 2001). Despite some initial success, the lack of additional studies suggests this method is no longer considered valid. The dose history of heated flint, however, begins with the time of heating. Dating heated flint by thermoluminescence (TL) is well established. Efforts to use ESR have been less successful. The quartz-based E' signal used for dating must be extracted from a complex spectrum derived from other minerals and organic inclusions. Its behavior depends somewhat on the heating temperature (Toyoda et al. 1993). If the heating temperature was over about 650 °C, a phase transition prevents the regrowth of the signal. Perhaps most problematic, there is a base “unbleachable” signal (to use the TL terminology) which varies from sample to sample (Skinner and Rudolph 1997). Thus neither the precision nor the accuracy of dating by ESR can match that of TL.

In a related study, heated quartz grains were dated to establish the age of a Lower Paleolithic site in Brittany (Monnier et al. 1994).

Last, but far from least, is the use of the E' signal to study the movement of earthquake faults. Along with the study of speleothems, this was one of the earliest applications. The principle is that the movement of an earthquake fault anneals radiation damage in quartz grains primarily by heat and pressure. Thus the observed modern dose reflects the age since last faulting event. Results may be affected by incomplete resetting – large grains may retain some of the original signal (Buhay et al. 1988). As well as the E' center, signals attributed to germanium, aluminum, titanium and the “OHC” center have been studied. The Ge signal has a short lifetime (in terms of this type of study), estimated to be 100 ka. As noted for the optical bleaching, the Ti center is less stable than that for Al. While good concordance of ages from different centers has been observed, the ESR ages can exceed the geological estimates, presumably due to incomplete resetting (Ikeya 1993). Other studies have agreed better with geology (Fukuchi et al. 1986).

Sulfate Minerals

Gypsum (calcium sulfate) is found in a number of environments as the result of precipitation or evaporation. Sulfite radicals have well-characterized g-values around $g = 2.004$. This is, unfortunately, the same region as the carbonate spectra, so natural gypsum may show both. A second signal at $g = 2.008$ can also be used for dating (Kasuya et al. 1991). Although the mean lifetime appears to exceed 10^{12} years, applications to date have concentrated on the time period <500 ka. They include additional efforts to study tectonics (Mathew et al. 2004). However, a comparison of ESR and TL ages showed consistent underestimation by ESR relative to TL, tentatively ascribed to uncertainty in the relative efficiencies of α -, β -, and γ -radiation in inducing defects (Nambi 1982).

In an interesting extension of ESR dating to other regions of the earth, barite (barium sulfate) dating has elucidated some aspects of hydrothermal vent formation in the depths of the ocean. Although the calculations are extremely complex, due to the shape of these vents, the proof of concept is encouraging (Sato et al. 2011).

Table 2 Materials commonly used in ESR dating. The first column notes whether the material has a signal that is either zero at $t = 0$ or determinable. The second notes whether this signal grows in a predictable manner so that an accumulated dose can be established. Finally the third column notes whether the signal stability is adequate for practical uses. The reliability of ages has been cross-checked by other methods for these materials as well. The greater the number of emoticons (positive or negative), the more confidence in the opinion

	Signal	AD	Age
Carbonates			
Coral	😊😊😊😊	😊😊😊	😊😊😊
Mollusk	😊😊	😊😊	😊😊
Speleothem	😊😊	😊😊	😊😊
Travertine	😊	😊😊	
Foraminifera	😊	😊	😊😊
Caliche	😊	😊	😊😊
Hydroxyapatite			
Tooth	😊😊😊😊	😊😊😊	😊😊😊
Bone	😊	😊	😊😊
Silicates			
Sediment			
E'	😊😊	😊😊	😊
Al, Ti,	😊😊	😊😊	😊
Faults, E'	😊😊	😊	😊
Chert, E', Al	😊😊	😊😊	😊😊😊

Space Science

Ikeya (1993) championed the concept of using ESR dating to study formations on the outer planets, using the $\text{OH}^\cdot$ radical. While too unstable to be measured at ambient Earth temperatures, he believed that the low temperatures in space would allow one to measure an accumulated dose. He did not think that this technique would be ready for use in less than a century, however.

Non-radiolytic Dating

So far we have discussed only free radicals created by radioactivity. In principle, any increase in free radical concentration with time could be used for dating. Oxidation of natural products also creates radicals. Ikeya and coworkers experimented with some preliminary work on organic degradation due to light and/or oxygen. Among the substances tested were oils on potato chips, and blood. In general, however, the signal lifetimes and saturation behavior severely limit the dating potential. A comprehensive review can be found in Ikeya (1993). There has been essentially no further work in this type of application since then.

Summary

This outline by no means exhausts the efforts that have been made to use ESR for dating. The following table can be used for an overview of the current state of ESR dating. It is, naturally,

oversimplified, but generally indicates what materials have been good sources for dating sites and which have serious flaws (Table 2).

A literature search will soon show that aside from the examples quoted above, many other minerals have been tested for their ESR response to radiation. Dating applications are the result of low dose rates delivered over a long period of time. Another major use of ESR for radiation sensitivity is determining high doses delivered over a short period of time, as in accident dosimetry. Since in this latter case signal stability is not an issue, useable materials abound. The future will undoubtedly demonstrate that some of these may be transferrable to the dating category. Certainly there is plenty of scope for experimentation; no scientific field should ever be considered closed.

Cross-References

- ▶ [Electron Spin Resonance Dating, Sediment](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating, Corals](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating, Teeth](#)
- ▶ [Electron Spin Resonance Spectrometer](#)
- ▶ [Radiation and Radioactivity](#)

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Luminescence, Coastal Sediments

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Definition

Luminescence. Light emitted by an irradiated semiconductor during exposure to light or heat. The light intensity emitted by the semiconductor is a function of the absorbed dose.

Luminescence dating technique. Dosimetric technique which determines the amount of absorbed dose in a dosimeter (semiconductor) such as quartz and feldspar and the rate of dose to which the dosimeter was exposed before the moment of sampling.

Coastal sediments. Deposits in the zone near where land and sea meet.

Introduction

Luminescence dating technique relies on the absorption of radiation dose in siliciclastic minerals such as quartz and feldspar. When the grains of these minerals are exposed to daylight for a sufficient length of time during sediment transport and deposition, the luminescence clock of the dosimeter is reset to zero. Besides sufficient resetting, the accuracy of a luminescence age of a coastal deposit depends upon sediment composition, the nature of wetting and drying, and the degree of postdepositional geochemical alterations. In general, the coastal environment is governed by the sea level. In the past, shelf areas have experienced migrating shorelines and associated deposits are today submerged unless the rate of uplift of land is faster than the rate of sea-level change or the sea level was, at the time, higher than today. During glacial periods, the sea level was low (e.g., ~120 m b.s.l. during MIS 2) and was situated at or below the shelf edge, causing subaerial processes to dominate the modern coastal area. During interglacial periods, the sea level was high, but, with the exception of the last interglacial, rarely as high as it is today. Thus, coastal sediments deposited at times of sea-level lowstand (e.g., MIS 2) are rarely uncovered. Likewise, coastal sediments deposited at times of maximum transgression (e.g., MIS 6/5.5) can be hard to find in localities where high rate of sea-level rise exceeds the sedimentation rate at the shoreline. Given the limited dose that luminescence dosimeters can accumulate and the preservation potential of coastal deposits, luminescence ages of coastal deposits are generally <300 ka, and within this range, we should mainly find ages of times when the sea level was at its maximum height and when it was falling.

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Table 1 Conceptual frame of tidal and wave processes and the link to daylight exposure of sediment grains (Mauz et al. 2010)

Process	Tide	Wave	Daylight exposure
Intertidal exposure	N/A	N/A	Unrestricted, with the exception of pools. Bleaching limited to surface few millimeters, depth being dependent upon grain-size distribution (reduced sorting, reduced penetration)
Early flood tide, sediment reworking by waves in advancing surf zone	Negligible waxing	Significant wave action causing sediment resuspension. High-frequency fluctuation in turbidity (higher during breaking, lower during shoaling and post-breaking)	Effectiveness determined by location relative to wave breakpoint – higher efficiency in swash zone, lower in surf zone, lowest in zone of wave shoaling
Flood tide, sediment transport within water column and along bed	Significant tidal currents orientated onshore (generally fastest at mid-tide). Finer sediments carried in suspension and intermittent suspension, coarser fraction transported as traction load	Negligible	Effectiveness reduced with depth through the water column, determined by turbidity (suspended sediment concentration). Bleaching efficiency significantly limited for traction load
Late flood tide/slack water, particle settling linked to grain size and flocculation	Waning-negligible	Some wave action in shallow water (depth < wave base)	Effectiveness determined by water depth (i.e., location/altitude on the tidal flat relative to high water) and residual turbidity. Bleaching likely to be more effective for fines retained in water column, but the sedimentation potential for these grains is limited
Ebb tide, potential for bed sediment resuspension and reworking	Waxing-significant tidal currents orientated offshore. Extent of ebb-current reworking linked to location/altitude on the tidal flat – limited on upper part and improved on lower part where ebb currents have sufficient time to gather speed and entrain bed sediment. Finer sediments carried in suspension and intermittent suspension, coarser fraction transported as traction load	Negligible	Effectiveness reduced with depth through the water column, determined by turbidity (suspended sediment concentration). Bleaching efficiency significantly limited for traction load
Shallow-water wave reworking as ebb tide shoreline leaves the tidal flat	Negligible	Significant wave action causing sediment resuspension. High-frequency fluctuation in turbidity (higher during	Effectiveness determined by location relative to wave breakpoint – higher efficiency in swash zone, lower in surf zone, lowest in zone of wave shoaling

(continued)

Luminescence, Coastal Sediments, Table 1 (continued)

Process	Tide	Wave	Daylight exposure
		breaking, lower during shoaling and post-breaking)	

Bleaching

Parameters controlling the degree of bleaching in coastal environments are length of daylight exposure at a given water depth, water turbulence, flow regime, and suspended sediment concentration (SSC). In 4 m turbid water, sunlight shorter than 500 nm and longer than 700 nm is almost completely attenuated (Berger and Luternauer 1987), and at 0.05 g l⁻¹ suspended sediment concentration (SSC), feldspar grains are virtually unbleached after 20 h exposure to light (Ditlefsen 1992). In an estuarine environment, light levels are reduced by three orders of magnitude in the upper 80 cm of the water column (Richardson 2001) due to the presence of SSC. But given that accurate ages were obtained from tidal environments, it was concluded that reworking of sediments through subsequent tidal cycles is crucial for sufficiently resetting the OSL clock (Madsen et al. 2007; Mauz et al. 2010). Table 1 shows that, when combined, the influences of transport and deposition processes, the interaction of tide- and wave-induced sediment transport, and the efficacy of subaerial exposure during low water dictate a high level of spatial and temporal variability in the degree of bleaching. It is good practice to study the suitability of a coastal environment for luminescence dating by examining the residual dose in modern samples (e.g., Brill et al. 2012). However, residual dose data are typically affected by large uncertainties which might impact on the assessment of samples with low doses.

Postdepositional Alteration

In general, any reorganization of the sediment, albeit small, is undesired in luminescence dating because it affects the mineral grains in terms of spatial distribution (Cunningham et al. 2012) and chemical pristineness in a largely unknown manner. Reorganizational processes that may affect the accuracy of the dating result are weathering, lithification, and bioturbation, where the first two are a consequence of wetting and drying and the latter depends on the biological activity in the coastal zone. Wetting and drying as a result of tidal cyclicity was studied by Roberts and Plater (2005) who compiled a readily applicable water-content model based on particle-size distribution, pore-space saturation, and inundation period. Wetting and drying as a result of climate seasonality was studied by Nathan and Mauz (2008) who addressed precipitation of carbonate in the pore space when the deposit falls dry. Mauz et al. (2009) report a 2–32 % reduction of dose rate for samples with significant carbonate content. Another challenge is represented by mollusc shells (Zander et al. 2007) and evaporitic sediment components (e.g., gypsum). These adsorb dissolved ²³⁴U from coastal water that typically deviates from the open ocean with regard to ²³⁴U/²³⁸U activity (see Ivanovich and Harmon (1992) for details on U-activity in ocean waters and uptake process). In this way, these components change the dose rate during burial and create large equivalent-dose over-dispersion (σ_b ; Galbraith and Roberts 2012). Rather unstudied so far is unsupported uranium in organic-rich tidal sediments (Bailiff and Tooley 2000) and in Fe and Mn oxyhydroxide coatings on the surface of mineral grains. Madsen et al. (2005) assume that it is negligible because the

contribution of uranium to the total dose rate of sand-sized dosimeters is rather small. Jeong et al. (2007) show how chemical processes like illuviation and leaching occurring under tropical climate conditions result in mixing of mineral grains, change of dose rate, and, ultimately, inaccurate ages.

Approaches to Dating

Jacobs (2008) reviews 196 studies on coastal and marine deposits originating from Europe, North Africa, South Africa, Australia, New Zealand, and North America. Few attempts were made for Scandinavia, west coast of Africa, East Africa, Arabia and India, southeast Asia and northeast Asia, South America, and the Arctic and Antarctic coasts (Jacobs 2008) reflecting the dominant application of the dating technique to soft sediment coasts outside arid and (formerly) glaciated environments.

Microtidal Sediments

As shown by Jacobs (2008), the majority of studies used soft sediment samples derived from mid-latitude beaches, deltas, barriers and foredunes, marine terraces, and beach ridges. These sediments are deposited in shallow, relatively clear water, often composed of well-sorted and well-bleached siliciclastic sand. They can be dated with high accuracy and precision (e.g., Thomas et al. 2008) even if the sand is young (e.g., Sawakuchi et al. 2008; Costas et al. 2012; Shen and Mauz 2012).

Indurated (hard) coastal sediments (e.g., beachrock) are usually well-bleached but may present problems with regard to dose rate. Most studies assume constant dose rate over time in an infinite matrix (e.g., Jacobs and Roberts 2009; Thiel et al. 2012). This is a fair approach for “old” samples where the uncertainty associated with the estimation of high doses exceeds the inaccuracy associated with the constant dose-rate assumption. For Holocene beachrock samples, however, Thomas (2009) obtained quartz OSL ages that seem to be underestimated, probably due to an overestimated dose rate.

Tidal Sediments

By outlining the conceptual frame and analyzing samples derived from a well-established stratigraphic framework (North Sea; 53°N), Mauz et al. (2010) find accurate as well as inaccurate quartz OSL ages and conclude that well-bleached samples may be obtained from all tidal sub-environments. For the same area, Fruergaard et al. (2011) present similar results which include few age overestimations derived from tidal channel samples. For quartz fine-silt samples originating from a west Korean mudflat (34°N), Kim et al. (2012) obtained ages in stratigraphic order between ~19 ka and ~1 ka. Also, Mauz et al. (2010) show that quartz fine silt from mudflats yields overestimated ages possibly due to high turbidity of the coastal water alongside little opportunities for tidal reworking. Even more challenging are coastal sediments from arctic coasts because transport distances are short, the coastal water is very turbid, and reworking opportunities are limited to the brief polar summer. Despite these conditions, Alexanderson and Murray (2012) found negligible residual doses in surface samples collected from up to 10 m water depth.

Gravel Beach

Conglomeratic deposits of gravel beaches are a challenge for luminescence dating. Not only are sand-sized mineral grains rare, the sediment matrix and geometry are inhomogeneous and standard assumptions (e.g., infinite matrix, homogeneous distribution of radio sources) do not apply. Mellett et al. (2012) avoided these problems by using the sandy matrix of deposits that contained exclusively limestone gravel of low radioactive element content. Jeong et al. (2007) show that gravel deposited in a tropical environment yields inaccurate OSL ages. Simms et al. (2011) used the underside of cobbles with which the clast rests on the beach surface. This approach assumes that the clast was rotated by wave action the last time before the relative sea level fell and was not moved by any environmental activity afterwards. The results from this study are in agreement with the local relative sea-level curve and hence encouraging.

High-Energy Coastal Deposits

High-energy events on coasts are storm surges and tsunamis, eventually lying down washover fan deposits or sand layers of various thicknesses which are distinctively different to the background sediments. Brill et al. (2012) estimated the residual dose in tsunami sand deposited during the Asian earthquake in 2004 to ~40 years, and Cunningham et al. (2011) found negligible quartz residual doses in storm-surge deposits. Sawakuchi et al. (2012) use OSL sensitivity (i.e., OSL signal intensity per unit dose) as a tracer to reconstruct frequency of storm impact on a coastal barrier on the basis of known sediment pathways on the coast. Analyzing washover fan deposits resulting from hurricane strikes, Davids et al. (2010) obtained consistent ages for feldspar and quartz separates indicating sufficient bleaching during such a high-energy event.

Summary

Most coastal deposits are sufficiently bleached and can be dated with high accuracy and precision owing to wave and tidal reworking and homogeneous sediment texture. Exceptions may be deposits laid down under high energy and in turbid water. Inaccuracies, if any, are mostly induced by dose-rate issues such as heterogeneous radiation field in gravel deposits, unknown initial U-activity, and changing dose rate in weathered or lithified deposits.

Cross-References

- [Luminescence Dating](#)
- [Luminescence Dating, Dose Rate](#)

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1 Molluscs, Foraminifera, and Other Carbonate Fossils

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4 Definitions

5 **Mollusc:** any member of the Phylum Mollusca. The Mollusca form a diverse group of ~ 85,000 extant
6 species, including Bivalvia (clams, oysters, mussels, scallops, etc.), Gastropoda (snails, slugs),
7 Cephalopoda (octopus, squid, cuttlefish, nautilus, ammonoids, etc.), Polyplacophora (chitons),
8 Sacophopoda (dentilids), Rostroconchia (all extinct), Monoplacophora, and Aplacophora. In the shell,
9 calcium carbonate, as aragonite, low or high magnesium calcite, reinforces a conchiolin (protein) and
10 chitin matrix.

11 **Barnacle:** any of several species of Arthropoda belonging to the Subphylum Crustacea, Infraclass
12 Cirripedia. Among the 1,220 or so species, most are encrusting filter- or suspension-feeding organisms.
13 Although some live as deep as 600 m, about 75% live at depths < 100 m in marine ecosystems, and 25 %
14 inhabit the intertidal zone. Within the intertidal zone, species inhabit a very restricted range of water
15 depth, allowing them to be used to mark paleosealevels with some accuracy. Infamous for fouling ships,
16 docks, and intertidal rocks, barnacles have plates that allow them to close off the internal shell to prevent
17 desiccation.

18 **Foraminifera** (abbreviation: **foram**): any member of the Phylum Foraminifera, a group of marine
19 amoeboid Protista. The Foraminifera comprise both extinct and extant species that all have thin
20 pseudopoda that form an external net for gathering food. Many species are planktonic, but several benthic
21 species live on the deep ocean floor, and a few species can tolerate brackish water.

22 **Carbonate compensation depth (CCD):** the depth at which all carbonate fossils have dissolved from
23 deep marine sediment. The aragonite compensation depth varies from that for calcite. Currently, the
24 depths vary from about 4,200 to 5,000 m, depending on the temperature, pressure, and the amount of
25 dissolved CO₂. In the past, the depths have varied dramatically, especially during the Quaternary.

26 **Aragonite:** a calcium carbonate (CaCO₃) mineral found in speleothems, travertines, carbonate cements
27 in sedimentary rocks, and live and fossilized shelled organisms, like molluscs and barnacles. Aragonite
28 often occurs as acicular crystals in speleothems, travertine, and carbonate cements, but in fossils, it may
29 take other crystal forms.

30 **Calcite:** a calcium carbonate (CaCO₃) mineral found in some speleothems, travertines, carbonate
31 cements in sedimentary rocks, and live and fossilized shelled organisms, like some molluscs. Calcite can
32 occur as rhombohedral crystals if allowed to grow uninhibited, but in fossils, it may take other crystal
33 forms.

34 **Irradiation ramping:** a technique used for very small samples in which only three to eight aliquots are
35 used to build a growth curve. After reading the spectra following the first set of irradiations, about half of
36 the aliquots are reirradiated to higher doses and the spectra for all the aliquots are reanalyzed, using the
37 aliquots that have not been reirradiated to calibrate the spectra for all the newly irradiated samples.
38 Normally, the 0 dose and at least one other aliquot are not reirradiated. The ramping can be repeated as
39 many times as necessary to build the growth curve. Normally, at least 10 different added doses are needed
40 to build a precise growth curve, but as many as 15–20 doses are commonly used in ramping.

41 **Ramped box model:** a model for deriving time-averaged cosmic and sedimentary doses for electron
42 spin resonance (ESR) dating first suggested by Deely et al. (2011). The model uses a series of time-limited

boxes whose end points have fixed dose rates derived from geological, paleontological, or biological criteria that define the sediment cover thickness and water depth. Within the intervening time period, the dose rates are assumed to change at a constant rate.

Introduction

In marine and lacustrine sedimentary units, open-air spring deposits, karst fissure fills, and caves and dating molluscs, foraminifera, barnacles, or other carbonate fossils found in the sediment (Table 1) can provide diverse information for Quaternary archaeological, paleontological, or geological studies. Electron spin resonance (ESR) dates for molluscs and planktonic foraminifera have provided vital geological and paleontological information. More recently, several researchers have used terrestrial molluscs to develop sealevel curves, monitor tectonic uplift, monitor water availability in the desert, and date archaeological finds. New developments in the field include applications for benthic foraminifera and barnacles.

ESR Dating Issues

Although molluscs and some other carbonate fossils can act as moderately open systems for U uptake, the minor discordance between the measured $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ ratios suggests that most U uptake accompanies sedimentation early in their depositional histories. Moreover, given the amount of U they normally absorb, the difference between the EU (early uptake) and LU (linear uptake) calculated ages for most molluscs and foraminifera is usually insignificant compared to their associated uncertainties.

Most ESR analyses on molluscs, foraminifera, barnacles, and other marine shells use the X band, but K band has been applied to molluscan aragonite for dating (Kinoshita et al. 2002). The techniques have also been expanded to recognize irradiated shell for retrospective accident dosimetry and dosimetric monitoring for the food industry (e.g., Ikeya et al. 1984; Nakajima et al. 1993; Raffi et al. 1996).

Aragonitic shells normally show five ESR peaks (Fig. 1; see also Blackwell 1995, Table 2), but calcitic shells have more complex spectra. For the peaks at $g = 2.0018$, 1.9976 , and 2.0007 , trap density is related to Mg/Ca ratios (Mudelsee et al. 1992), which can change with diagenesis, secondary mineralization, and fossilization, making them unsuitable for dating some species. Generally, either the peaks at $g = 2.0014$ and 2.0007 in calcitic shells or the peak at $g = 2.0007$ in aragonitic shells are the most reliable, but that must be tested for each species individually, because complex peaks do occur and peaks other than that at $g = 2.0007$ may be light sensitive in some species (Bartoll et al. 2000). Secondary mineralization can cause interference that affects the accumulated dose ($\mathcal{A}_\Sigma$) measurement and age calculation. Signal lifetimes vary significantly depending on the peak and species (e.g., see references in Blackwell 1995, Table 2). Some species show inflection points in their growth curves, such as the peak at $g = 2.0018$ in *Anadara*, *Katylesia*, *Dorax*, and *Phalium*, making it difficult to select an appropriate set of added doses for measuring $\mathcal{A}_\Sigma$ (e.g., Brumby and Yoshida 1994; Shih et al. 2002). Schellmann and Radtke (2001) advocated using a plateau technique with 40–60 irradiation steps to maximize accuracy in the growth curves. They successfully applied that technique to dating coastal marine units in Patagonia (Schellmann et al. 2008). Dului (2000) showed that the aragonite cuttlebone in cuttlefish preserved measureable signals.

Petrographic, X-ray diffraction (XRD), or geochemical analyses should accompany any ESR date on carbonate fossils or travertines to avoid remineralized and recrystallized samples. Contamination from Mn peaks often requires overmodulation to discriminate the dating peaks. Due to U uptake, modeling may

Table 1 Carbonate samples database by ESR

Sample type	Minerals ¹	Zeroing req'd?	Isochrons possible? ^a	Ramping possible? ^b	Species effects? ^a	Best type or species?	Minimum sample for standard ESR ^{c,d} (mg/subsample)	Effects from diagenesis, secondary mineralization, or cementation			Grinding effects?	
								Signal intensity	Interference?	Inaccurate ages?		
Molluscs	cct, argt	No	Unknown	Up to 6 rampings	Yes	Terrestrial or marine	50–100 ^{e,f}	May increase	Likely	Possibly	N/a	Interference
Coral, echinoderms	argt	No	Theoret	Up to 6 rampings	Yes	Densest, uneroded	50–100 ^{e,f}	May increase	Likely	Possibly	N/a	Interference
Foraminifera, both planktonic & benthonic	cct, argt	No	Unknown	Up to 10 rampings	Unknown	Planktonic or benthonic	100–200 ^{c,f}	May increase	Likely	Possibly	N/a	Interference
Ostracodes	cct, argt	No	Unknown	Unknown	Unknown	Unknown	100–200 ^{c,f}	May increase	Likely	Possibly	N/a	Interference
Cuttlefish cuttlebone	argt	Unknown	Unknown	Unknown	Unknown	Unknown	100–200 ^{c,f}	Unknown	Unknown	Unknown	Unknown	Interference
Ratite egg shells	cct	No	Theoret	Unknown	Unknown	Unknown	50–100	May increase	Likely	Possibly	N/a	Interference
Travertine, speleothem	cct, argt	No	Yes	Unknown	N/a	Densest	50–100 ^{g,h}	May increase	Likely	Possibly	N/a	Interference
Calcrete, caliche, stromatolites	cct	No	Unknown	Unknown	N/a	Densest	50–100 ^{g,h}	May increase	Likely	Possibly	Yes, if clasts CO ₃ also	Interference
Authigenic cement	cct, argt	No	Unknown	Unknown	N/a	Densest	100	May increase	Likely	Possibly	N/a	Interference

^aAbbreviations: cct calcite, CO₃ carbonate, argt aragonite, *theoret* theoretically.

^bIrradiation ramping technique involves reirradiating some aliquots, but can take up to 2 years to complete for 8–10 rampings. The number indicates the maximum number of rampings that could be required for small samples.

^cSizes assume little or no diagenesis is present. For diagenetically altered samples, larger samples are needed.

^dFor isochron analysis, the sample size must be increased by a factor of 5–8.

^eFor species that have not been tested for ESR applicability, another 100–200 g is necessary for stability and other background tests.

^fSmaller species may require special techniques or mixing multiple individuals into one subsample.

^gLarge sample sizes ensure sufficient pristine mineral for analysis after mineral separation and for XRD or petrographic analysis to check for recrystallization.

^hFor samples from new study sites or sample types not yet tested for ESR applicability, another 100–200 g may be necessary.

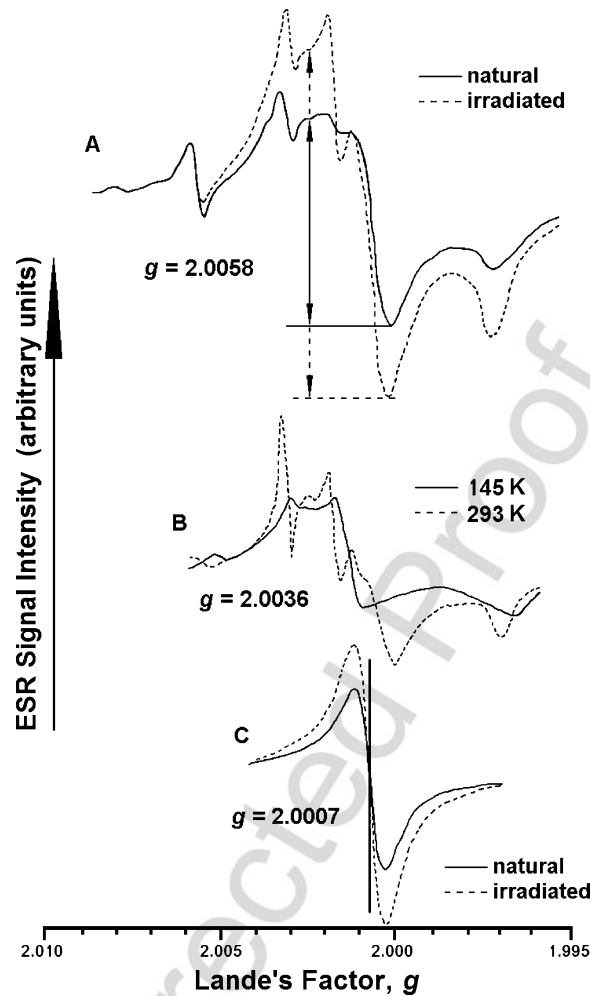


Fig. 1 ESR spectra in aragonitic mollusc shells. Three signals commonly can be used for dating in aragonitic mollusc shells (adapted from Blackwell 2006): (a) The signal at $g = 2.0058$ before and after irradiation measured at room temperature. (b) The signal at $g = 2.0036$ measured at room temperature (293 K) and at 145 K. (c) The signal at $g = 2.0007$ before and after irradiation measured at room temperature.

be required for uraniferous samples that cannot be analyzed by coupled ESR- $^{230}\text{Th}/^{234}\text{U}$ dating. In some fresh and hypersaline systems, the $(^{234}\text{U}/^{238}\text{U})_0$ ratio may also need to be measured or modeled. For each species and signal, the α efficiency factor, κ_α , must be measured. Long-term signal fading may also need to be considered, depending on the peak selected and its thermal stability (see Blackwell 1995, Table 2).

Molluscs and barnacles found in life position give the most reliable dating results, although that does not guarantee that reworking has not affected the unit. Larger species are preferred so that each subsample represents a single individual (Table 1), but several shells can be combined from smaller species, assuming that none have been reworked. Fragmentary samples still need to be speciated. Since species effects do occur, analyzing two or three different species from each unit can increase the dating precision and accuracy. Good agreement between ESR, TL, OSL, ^{14}C , and AAR (amino acid racemization) ages has occurred in studies with *Hendersonia* and *Allogona* using $g = 2.0007$ (Skinner and Mirecki 1993) and in *Lymnaea ballica* and *Cerastoderma glaucum* using $g = 2.0012$ (Molod'kov 1996). Thermal stabilities in *Monauha caucaicala* significantly exceeded those in many marine molluscs. For untested species, ~ 100 g of pristine shell are needed to perform the necessary signal stability and calibration tests.

t2.1

Table 2 Tests for reworked snails from Medauwara, Kharga Oasis

Sample	Description	$[U_{\text{mol}}]^a$ (ppm)	Accumulated dose, $\mathcal{A}_\Sigma$ (gray)	Age ^{a,b} LU (ka)
a. Big Snail Gully				
RM47	Grab sample	0.66	67.8	104.1
KAR17		± 0.02	5.3	9.2
RM51	Grab sample	0.76	61.0	94.1
KAR17c		± 0.02	2.2	5.2
RM54	Grab sample	0.75	58.6	90.1
KAR17b		± 0.02	2.9	5.9
RM53	Grab sample	0.67	62.3	95.9
KAR17a		± 0.02	3.3	6.5
RM52	Grab sample	0.81	68.7	105.5
KAR17d		± 0.02	4.0	7.6
b. Railway 3				
FM85	Unweathered	7.46	29.5	24.0
KAR105e		± 0.02	1.6	3.0
FM84	Light, rugose	25.97	56.5	31.8
KAR105d	Unweathered	± 0.02	3.1	2.8
FM82	Dark, rugose	15.34	42.8	34.4
KAR105b	Unweathered	± 0.02	4.2	5.1
FM83	Light, smooth	26.09	75.2	40.1
KAR105c	Weathered	± 0.02	3.4	5.3
FM81	Dark, smooth	11.52	57.3	50.2
KAR105a	Weathered	± 0.02	3.3	5.8
c. Parking Lot Basin				
FM77	Small, light, rugose	1.16	40.5	63.6
KAR102a	Unweathered	± 0.02	4.0	8.2
FM80	Medium, red-stained,	0.93	54.7	87.2
KAR102f	Rugose, unweathered	± 0.02	4.7	10.5
FM79	Medium, grey, smooth	1.06	42.4	67.1
KAR102e	Weathered	± 0.02	2.1	6.5
FM78	Medium, light, smooth	1.26	54.8	84.3
KAR102d	Weathered	± 0.02	4.6	10.0

^aAbbreviations:

LU assuming linear (continuous) U uptake, $p = 0$

$[U_{\text{mol}}] = U$ concentration in the molluscs

^bAges calculated using

α/γ factor, $\kappa_\alpha = 0.10 \pm 0.01$

initial U activity ratio, $(^{234}\text{U}/^{238}\text{U})_0 = 1.2 \pm 0.20$

aragonite density, $\rho_{\text{mol}} = 2.95 \pm 0.01 \text{ g/cm}^3$

radon loss from the shells, $Rn_{\text{mol}} = 0.0 \pm 0.0 \text{ vol\%}$

carbonate sediment density, $\rho_{\text{cal}} = 2.96 \pm 0.01 \text{ g/cm}^3$

quartz sediment density, $\rho_{\text{qtz}} = 2.66 \pm 0.01 \text{ g/cm}^3$

quartz sediment density, $\rho_{\text{qtz}} = 2.66 \pm 0.01 \text{ g/cm}^3$

cosmic dose rate, $\overline{D}_{\text{cos}}(t) = 0.293 \pm 0.010 \text{ } \mu\text{Gy/y}$

sedimentary water concentration, $W_{\text{sed}} = 10.0 \pm 5.0 \text{ wt\%}$

All errors are 1σ .

Data from Blackwell et al. (2012)

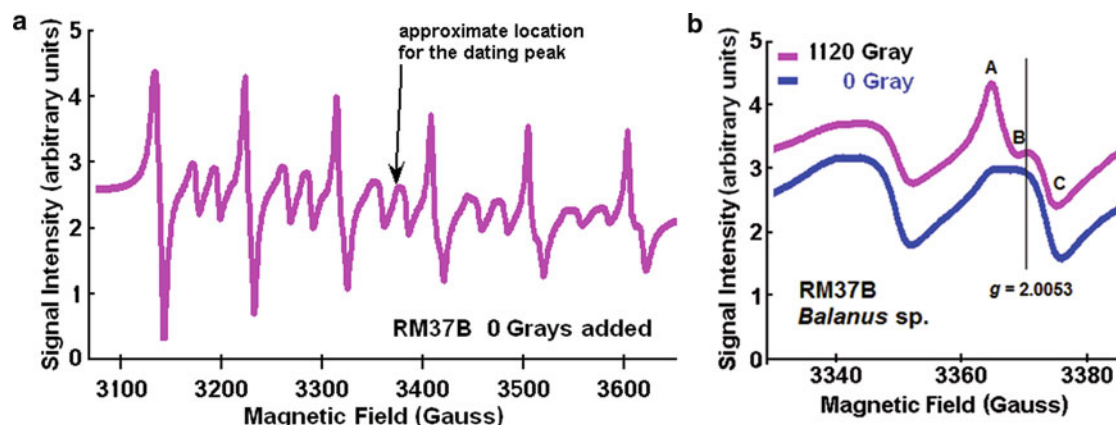


Fig. 2 Mn^{2+} interference peaks in barnacles. In RM37B, from Norridgewock, the Mn^{2+} signal completely obscured the unirradiated (0 krad) signal, making it impossible to measure peak heights at the lower added doses (adapted from Blackwell et al. 2010): (a) The Mn^{2+} interference peaks. In the natural sample, the Mn^{2+} signal exhibited its typically complex spectrum centered at $g = 2.0118$. Normally, Mn^{2+} has seven multiplets, but the seventh is off the spectrum to the right. (b) The dating signal at $g = 2.0053$. At higher radiation doses, such as with 112 krad, as shown here, the dating peak's signal height can be measured, but destructive interference may have reduced the height for the A peak, making the peak height measurement inaccurate.

For barnacles, diagenesis or signal interference may cause some samples to be unsuitable. For example, in barnacles from Norridgewock, ME, Mn interference prevented the peak heights from being read (Fig. 2; Blackwell et al. 2010). Similar interference problems can occur in molluscs or foraminifera. Iron contamination can also produce a very broad Fe^{3+} signal interference that tilts the baseline, thus, potentially adding a systematic error to any peak height measurements (Fig. 3; Blackwell et al. 2010). Both benthic and planktonic foraminifera can suffer diagenesis due to carbonate dissolution, if they sit below the carbonate compensation depth (e.g., Tadia et al. 2002). Since the planktonic foraminifera tests are larger, however, they persist longer in deep sediment and are considerably easier to pick from sediment cores. Nonetheless, both planktonic and benthonic foraminifera are datable (Sato 1981; Blackwell et al. 2013), although both may need irradiation ramping to measure enough doses to build the growth curves for these typically tiny samples. In molluscs, heating to temperatures slightly above 100°C can start to zero the dating signals, but do not affect the Fe or Mn signals, allowing the pure interference signals to be scanned and then removed by signal subtraction from the dating sample, a technique that drops the precision, but raises accuracy for the peak height measurements in contaminated samples. This correction is likely applicable to other contaminated sample types, but it remains to be tested.

Exactly how deep in time molluscs and foraminifera can provide reliable ESR dates remains something of an open question. Traditionally, most experts agreed that the range for molluscs tended to be about from $\sim 5\text{--}10 \text{ } \kappa_{\alpha}$ to as old as $\sim 500 \text{ } \kappa_{\alpha}$ (e.g., see references in Blackwell 1995, 2001, 2006), although Barabas et al. (1988) showed that the signal at $g = 2.0036$ in foraminifera exceeded 1 Ma. Dating samples on the young end is hampered by inability to recognize the dating signal in very young molluscs, while the old end is limited by diagenetic alteration and signal stability. Periodically, however, reports surface hinting that the range could be somewhat longer. For example, Vichaidid et al. (2007) reported ESR ages as old as 13 Ma for marine molluscs in Thailand. The reliability for ages this old must await tests for reproducibility or corroborating ages from another chronometer, particularly since overmodulating some aragonitic signals can produce apparently reliable growth curves without inflection points that hide multiple signals that each grow at different dose absorption rates, producing peaks with different lifetimes (stabilities), that can fade or anneal at different rates under different conditions. Blackwell et al. (2013) did report an age of

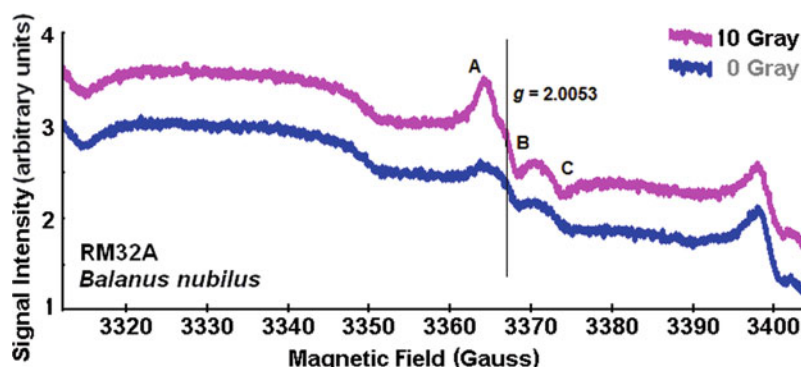


Fig. 3 Fe interference in barnacles. Barnacles have a radiation-sensitive peak at $g = 2.0053$. In RM32A from northern BC, shown here, the unirradiated (0 krad) signal grew regularly with irradiation, producing an identical irradiated signal. Interference from the Fe^{3+} peak caused the spectrum to have a consistently “tilted” baseline. Nonetheless, measuring the peak height from the top of the A peak to the base of the B peak did allow an age to be calculated, although the high signal-to-noise ratio in the lowest dose aliquots made measuring the peak heights difficult (after Blackwell et al. 2010).

2.29 ± 0.38 Ma for molluscs found encased from Kharga Basin, Egypt, with which Oldowan tools were associated, which suggested that the ESR age might be reliable.

Fossils can be easily reworked by sedimentary processes, such as erosion/redeposition or bioturbation, from older into younger depositional units (e.g., Blackwell 1994; Blackwell et al. 2012). Therefore, any sampling program should collect at least 8–10 samples from each stratigraphic unit or sequence of units to increase the chance that the samples analyzed provide dates related to the event of interest. Nominally, if 4–5 independent grab analyses from one bag of small or thin-walled molluscs or foraminifera all give the same age within errors, their age can probably be considered to date the unit’s deposition, as in Table 2a, for grab samples of *Melanoides tuberculata*. Tables 2b and 2c demonstrate that the weathering state or diagenetic features provides no clue to the ESR ages calculated (Blackwell et al. 2012). For larger shells, 4–5 independent ESR ages that agree well usually provide a reliable date for a given unit.

Although the required sample weight varies depending on the auxiliary analyses necessary (Table 2), the ESR analysis itself, and the associated NAA or geochemical analyses to measure the internal dose rate, require 1–2 g of pristine carbonate per standard ESR subsample. Secondary mineralization or cementation checks require larger samples, as do samples in which diagenesis may have occurred or samples needing to be separated into discrete mineral phases. Table 1 lists the minimum sample sizes normally needed for various sample types. For very small samples (100–200 mg), the irradiation ramping technique, in which several aliquots are reirradiated several times, can be used to get enough different doses to build a reliable growth curve. Irradiation ramping, however, does lengthen the total dating analysis time by up to 1–2 years, due to the special handling necessary.

Since isochron analysis for all samples, except teeth, is still experimental, either associated sediment samples should be collected for sedimentary geochemical analyses or the sampling locations need to be tested with in situ γ or TL dosimetry to ensure accurate dates. For TL dosimetry, the dosimetry site (i.e., the spot from which the samples were or will be removed) needs to be unaffected by further excavation or deflation for 6–12 months while the dosimeters are in place. Due to the high probability of equipment tampering or theft in lacustrine or coastal marine sites, where security can be impossible to maintain over long periods, either γ dosimetry or sedimentary geochemical analyses are preferred over TL dosimetry.

Water, rock, and sediment attenuate the cosmic dose reaching any sample below. Since many marine shells and some lacustrine molluscs are normally deposited in water, the water depth above the sample presents a potential source of systematic or random error in the analyses. For many samples, at some point, more sediment covers the fossil, while the water could disappear due to tectonic uplift, the lake drying, or

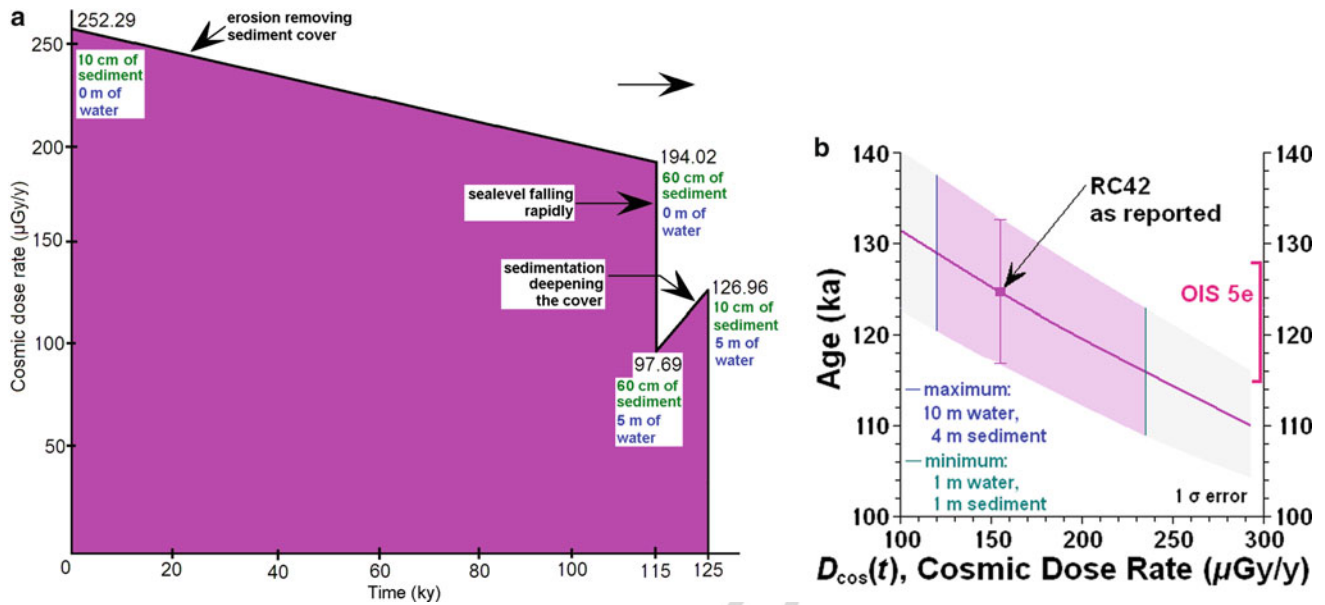


Fig. 4 Modeling the time-averaged cosmic dose rates, $\bar{D}_{\text{cos}}(t)$. To account for sedimentation and denudation, time-averaged cosmic dose rates, $\bar{D}_{\text{cos}}(t)$, must be modeled (adapted from Deely et al. 2011): (a) A ramped box model for the mollusc RM79, San Salvador: Instantaneous $D_{\text{cos}}(t)$ were integrated over time to calculate the time-averaged dose rate, $\bar{D}_{\text{cos}}(t)$. This model assumed that RM79 was deposited or lived in 10 cm of sediment under 5 m of water at 125 ka giving $D_{\text{cos}}(t) = 127 \mu\text{Gy/y}$. By 115 ka, another 50 cm of sediment had reduced $D_{\text{cos}}(t)$ to 98 $\mu\text{Gy/y}$. Then, sealevel was assumed to have dropped 5 m in a geologically instantaneous time, which raised $D_{\text{cos}}(t)$ to 194 $\mu\text{Gy/y}$. As the platform was denuded, thinning the sediment cover to 10 cm today, $D_{\text{cos}}(t)$ rose to 252 $\mu\text{Gy/y}$. (b) The effect of $\bar{D}_{\text{cos}}(t)$ on the coral RC42, San Salvador, assuming that its possible depth during growth ranged from 1 to 10 m, and its maximum sediment cover did not exceed 2 m more than its current cover of 1 m yielded ages that ranged from 121 to 128 ± 8 ka. All these ages correlated well with OIS 5e, the known age for the Cockburn Town Reef.

sealevel changes, making it necessary to model the cosmic dose rate changes with time in order to derive a time-averaged cosmic dose rate. For terrestrial molluscs, the speed at which sediment covers the sample must also be modeled to estimate the time-averaged sedimentary, as well as the cosmic, dose rates. In some areas, later denudation may remove the sediment cover, which again will affect both the sedimentary and cosmic dose rates. Several ways to model such changes exist. Deely et al. (2011) used a ramped box model (e.g., Fig. 4a) in which the end points of the ramped sequences were tied to modern analogue species' preferences for sediment or water depth, and to paleodepths and sediment cover thicknesses as estimated from geological observations. When tested, their modeling produced ESR ages that agreed well with known ages for corals from an MIS 5e reef (Fig. 4b). While more mathematically intricate models could be constructed, they likely provide little improvement in accuracy given the uncertainties in the paleowater or sediment cover depths and the time input required to do the modeling. After all, such models are only as accurate as the certainty about the geological conditions under which the sample was originally deposited, which can be sketchy at best for species in coastal plain, lacustrine, or terrestrial settings. For most situations, using time slices of 1 ky for such modeling exercises provides reasonable accuracy, but water and sediment cover depths need to be refined to within 0.1–0.5 m for molluscs deposited in shallow water and to within 1–2 m for species from deeper water up to 200 m (Deely et al. 2011). For species deposited under > 200 m of water or > 100 m of carbonate sediment, the cosmic dose rate is negligible.

174 Applications to Quaternary Studies

175 After Ikeya (1980) first described ESR signals in molluscs, Ikeya and Ohmura (1981), Radtke
176 et al. (1982), Baffa and Mascarenhas (1985), Katzenberger and Grün (1985), Hütt et al. (1983), and
177 Skinner (1986) were among the first researchers to report ESR ages for marine molluscs. They and their
178 colleagues all later applied these methods to problems such as dating (e.g., Dash et al. 2002; Kinoshita
179 et al. 2002) and then correlating coastal marine units (e.g., Mirecki et al. 1995; Schellmann et al. 2008)
180 measuring coastal uplift in tectonically active areas (e.g., Hantoro et al. 1994; Doğan et al. 2011; Tari
181 et al. 2013) or determining the magnitude of sealevel change in order to build paleosealevel curves in
182 tectonically stable areas (e.g., Molod'kov and Bolikhovskaya 2002; Deely et al. 2011). These methods are
183 now well established, although its application in each new study area requires that the tests for signal
184 stability in new species be completed before the dates can be assumed to be reliable. Such ESR studies are
185 often coupled with other applicable dating methods, although mid Quaternary deposits in many areas may
186 lack suitable samples for most methods other than ESR (e.g., Takada et al. 2003; Tari et al. 2013). For
187 more detailed discussions of molluscan dating applications, see Blackwell (1995, 2001, 2006).

188 Both terrestrial and freshwater molluscs can give reasonable ESR ages, depending on the species.
189 Molod'kov (2001) reported ages of 393 ± 27 ka for Layer 5b, for terrestrial molluscs preserved in the
190 Lower Paleolithic site at Treugol'naya Cave, Russia. These dates agreed well with ESR dates on herbivore
191 teeth from the same sequence (Blackwell et al. 2005). Given the inherent differences in the signals in these
192 two chronometers, this suggests that these terrestrial molluscs do give reliable ESR ages.

193 In late Pleistocene dune sequences on San Salvador Island, Deely et al. (2011) showed that the
194 terrestrial mollusc *Cerion* gave ESR dates that agreed with those obtained from corals in MIS 5 reefs.
195 They also used ESR ages on *Codakia*, a marine mollusc that inhabits a very restricted tidal and sediment
196 depth range, to pinpoint sealevel positions during Marine Isotope Stage 5.

197 After Sato (1981) first used ESR to date planktonic foraminifera, applications in pelagic marine
198 sediment have become routine (e.g., Hoffmann et al. 2003). Using ESR, a provenance study recognized
199 foraminifera in Cypriote-style limestone statuettes (Polikreti et al. 2004). Blackwell et al. (2013) used
200 ESR to date benthic late Quaternary foraminifera from the Cearà Rise, in the central Atlantic. Otamendi
201 et al. (2006) suggested that Fe and Mn^{2+} signals in Cretaceous to Eocene foraminifera could be used for
202 stratigraphy and paleoenvironmental reconstruction.

203 Summary

204 ESR dating for molluscs and foraminifera will likely continue to provide valuable geological and
205 paleontological dates that can help to answer questions regarding plate tectonic events, geohazard
206 potentials, volcanic histories, groundwater hydrology, Quaternary climatic and sealevel fluctuations,
207 Quaternary sedimentation and erosion, as well as dating archaeological sites and helping to estimate
208 species' first and last appearances. The future will likely see even more applications to groups of
209 organisms hitherto untested as well as innovative solutions to identify and correct interference problems
210 seen in some species.

211 Cross-References

- 212 ► [\$^{230}\text{Th}/^{234}\text{U}\$ Dating of Corals](#)
- 213 ► [\$^{230}\text{Th}/^{234}\text{U}\$ Dating of Marine Carbonates](#)

- 214 ► [²³⁰Th/²³⁴U Dating of Teeth](#)
- 215 ► [Carbonates, Lacustrine \(U-Series\)](#)
- 216 ► [Carbonates, Marine \(U-Series\)](#)
- 217 ► [Carbonates, Terrestrial \(¹⁴C\)](#)
- 218 ► [Electron Spin Resonance \(ESR\) Dating](#)
- 219 ► [Electron Spin Resonance \(ESR\) Dating of Coral](#)
- 220 ► [Luminescence, Biogenic Carbonates](#)
- 221 ► [Marine Isotope Stratigraphy](#)

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Archaeomagnetic Dating

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Definition

Archaeomagnetic dating is the study of the past geomagnetic field as recorded by archaeological materials and the interpretation of this information to date past events.

Introduction

Archaeomagnetic dating is a method for dating fired materials and sediments from archaeological sites, based on their preserved magnetic remanence. The principles of the method can be summarized as follows:

- The geomagnetic field changes significantly on archaeologically relevant timescales of decades and centuries (Tarling 1983, p. 145).
- Some archaeological materials contain magnetized particles, and certain events cause the geomagnetic field at a particular moment in time to be recorded by these particles.
- This recorded magnetization can be measured in the laboratory.
- By comparing the recorded magnetization with a dated record of changes in the geomagnetic field with time, the event which caused the recording can be dated.

The application of archaeomagnetic dating is restricted in time and location to regions where there is detailed knowledge of the geomagnetic field for the period in question. The strengths of archaeomagnetic dating are that it dates fired clay and stone, for example, hearths, kilns, ovens, and furnaces, which are frequently well preserved on archaeological sites; it dates the last use of features, providing a clear link to human activity; it can be cost-effective and is potentially most precise in periods where other dating methods, e.g., radiocarbon dating, are problematic.

The Physical Basis

Archaeomagnetic dating is based on a comparison of the past geomagnetic field, as recorded by archaeological materials, with a dated record of changes in the Earth's field over time in a particular geographical area. The geomagnetic field changes both in direction (declination and inclination) and in strength (intensity) (Lanza and Meloni 2006, p. 34), and archaeomagnetic dating can be based on changes in either direction or intensity or a combination.

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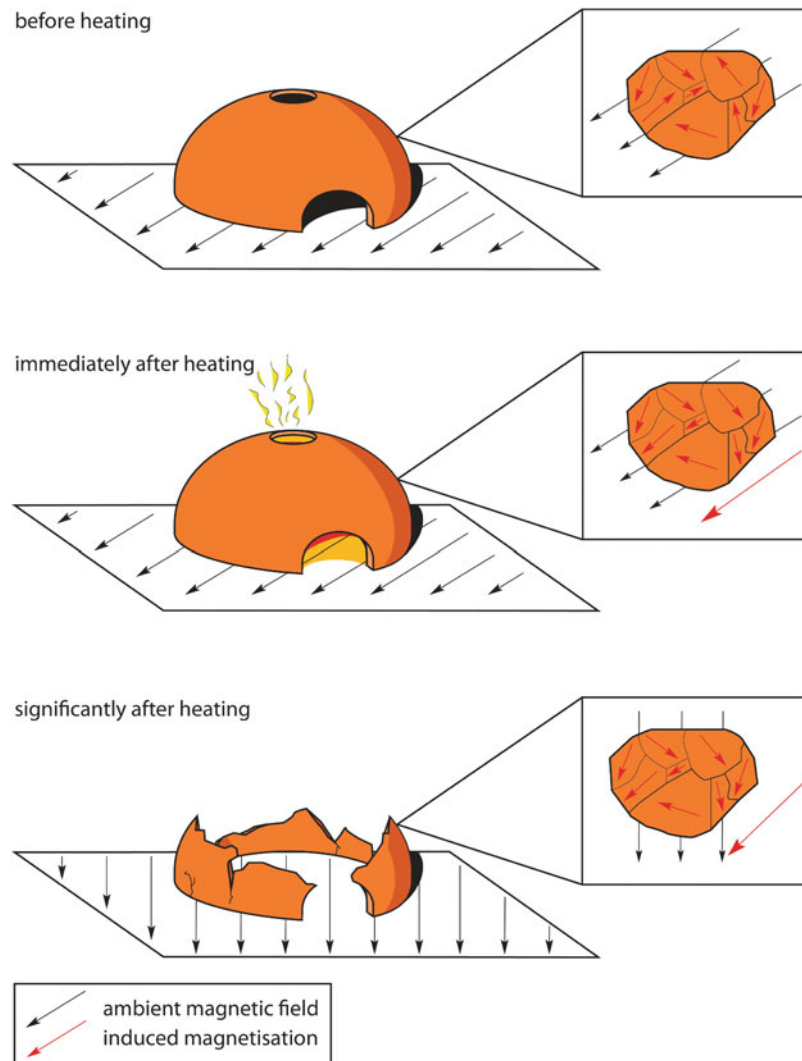


Fig. 1 The acquisition of thermoremanent magnetization. Before heating, the magnetic domains within the material are randomly orientated within the ambient field and cancel out. During heating, some domains gain sufficient energy to reorientate in the direction of the ambient field and retain this orientation on cooling, producing an induced magnetization. As time passes, the ambient field changes, but the magnetic domains retain the magnetization at the time of cooling (Adapted from Linford (2006), Fig. 2)

For archaeological material to be suitable for dating, it must contain sufficient magnetized particles, and an event must have caused these particles to record the Earth's magnetic field. Many geologically derived materials, e.g., soils, sediments, and clays, contain suitable iron oxides, such as magnetite, hematite, and maghemite (Merrill et al. 1998, p. 84). There are primarily two types of archaeological events which may result in the Earth's magnetic field at a particular moment being recorded by archaeological material: heating and deposition in water. If fired materials have been heated above the Curie temperature of the iron oxides (typically 650–700 °C), they easily become magnetized in the direction of the ambient field, which is usually the geomagnetic field (Fig. 1). On cooling, they retain this thermoremanent magnetization, which reflects the Earth's magnetic field at the time of last cooling. Suitable archaeological features include hearths, kilns, ovens, and other fired structures. Water-lain sediments may acquire a datable detrital remanent magnetization from the alignment of their magnetic grains by the ambient field

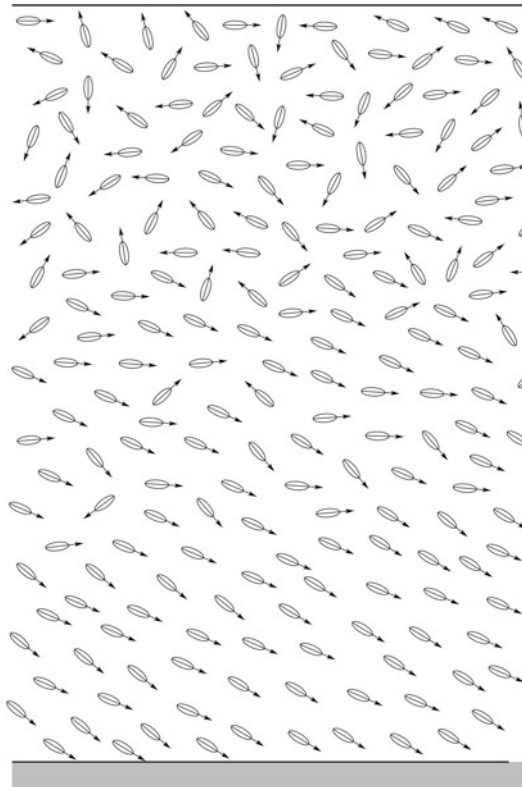


Fig. 2 The acquisition of detrital (or depositional) remanent magnetization. Some sediment particles may be weakly magnetized, usually along their long axes. As they settle through the water column, they are free to rotate and align with the ambient magnetic field. They retain this orientation on settling and become fixed in position by the weight of sediment accumulating above them. They are no longer able to rotate and retain the magnetic direction of the ambient field at the time they became locked in place (Adapted from Linford (2006), Fig. 3)

during deposition (Fig. 2). The magnetized grains then settle and become immobilized, retaining a record of the direction of the geomagnetic field at their deposition. This effect allows deposits in wells, ditches, and streams to be dated. However, uncertainty over the exact moment at which the magnetization is acquired (Evans and Heller 2003, p. 86) and postdepositional disturbance of the magnetization by bioturbation and diagenesis of sediments (Batt 1999) means that almost all archaeomagnetic studies focus on fired materials.

The Method in Practice

Archaeomagnetic dating by direction requires the exact position of the archaeological material to be recorded in relation to the present geomagnetic field, and so the material must be undisturbed and sampled in situ. Careful evaluation of structural remains is required to identify any post-firing movement and to select undisturbed areas for sampling. In addition, the magnetic field in which the feature cooled may be disturbed by the magnetization of faster cooling parts of the feature (Schurr et al. 1984). The presence of magnetic materials, such as iron slag (Abrahamsen et al. 2003), can also cause disturbance. Sometimes such disturbances are not visible on site but will be revealed by statistical analysis of the measurements of remanent magnetization, and so, where possible, different parts of the feature must be sampled and compared (Fig. 3). Samples of robust fired materials can be taken by coring, attaching plastic reference buttons using a fast-setting epoxy



Fig. 3 Archaeomagnetic sampling of a pottery kiln, showing samples taken by the button method from walls, floor, and pedestal

resin, or encasing samples in plaster of Paris before lifting (Linford 2006; Trapanese et al. 2008). Sediments and friable fired materials are sampled by insertion of plastic cylinders. Approximately 15 small (c. 1 cm³) samples are needed from each feature, and it may be possible to select sampling locations to minimize the visual impact. In all cases, the orientation of the in situ samples must be measured, usually by leveling the sample horizontally and marking the north direction using a magnetic or sun compass or a gyrotheodolite. Measurements of archaeointensity have the significant advantage that in situ samples are not required, allowing the dating of bricks from buildings or non-orientated pottery fragments (Shaw et al. 1999). These determinations can be carried out on much smaller samples, depending on the measuring instrument.

In the laboratory, the remanent magnetization of each sample is measured in a magnetometer, and the stability of this magnetization is evaluated by alternating magnetic field or thermal demagnetization (Merrill et al. 1998, p. 90). Demagnetization is necessary as the thermo- or detrital remanent magnetization acquired in the past may be overprinted by a viscous remanent magnetization, caused by magnetically soft materials changing with the geomagnetic field. The distribution of the stable magnetic components is assessed using Fisher statistics (Fisher 1953) to calculate a mean magnetic direction, together with its angular spread (α_{95}).

Dating by direction is relatively experimentally straightforward as the magnetic direction recorded by the sample is directly comparable to the past magnetic field direction. However, dating by intensity is more complex as the strength of magnetization of the sample is influenced not only by the strength of the past field but also by the mineralogical composition and firing regime (Merrill et al. 1998, p. 102). Laboratory techniques have been developed to correct for these factors (Gallet et al. 2009; Tauxe and Yamazaki 2007), but the determination of past intensity involves significantly more measurements than direction, and there are many more potential sources of uncertainty (Gallet et al. 2009). These challenges mean that many past studies have focused on magnetic direction; however, the determination of intensity is becoming routine, allowing definition of the entire magnetic vector (Sternberg 2001).

Having obtained the past magnetic field, the date is obtained by comparison with a secular variation record of changes in the Earth's field (Fig. 4). This record is compiled from direct measurements of the field, where available, and, prior to that, from archaeomagnetic measurements of features or sediments dated by other methods. As the field varies spatially, there needs to be sufficient data with 1,000 km (Noel and Batt 1990), and the development of secular variation records has been the subject of significant recent research. Early studies relied on a visual comparison of magnetic measurements with hand-interpolated calibration curves (e.g., Clark

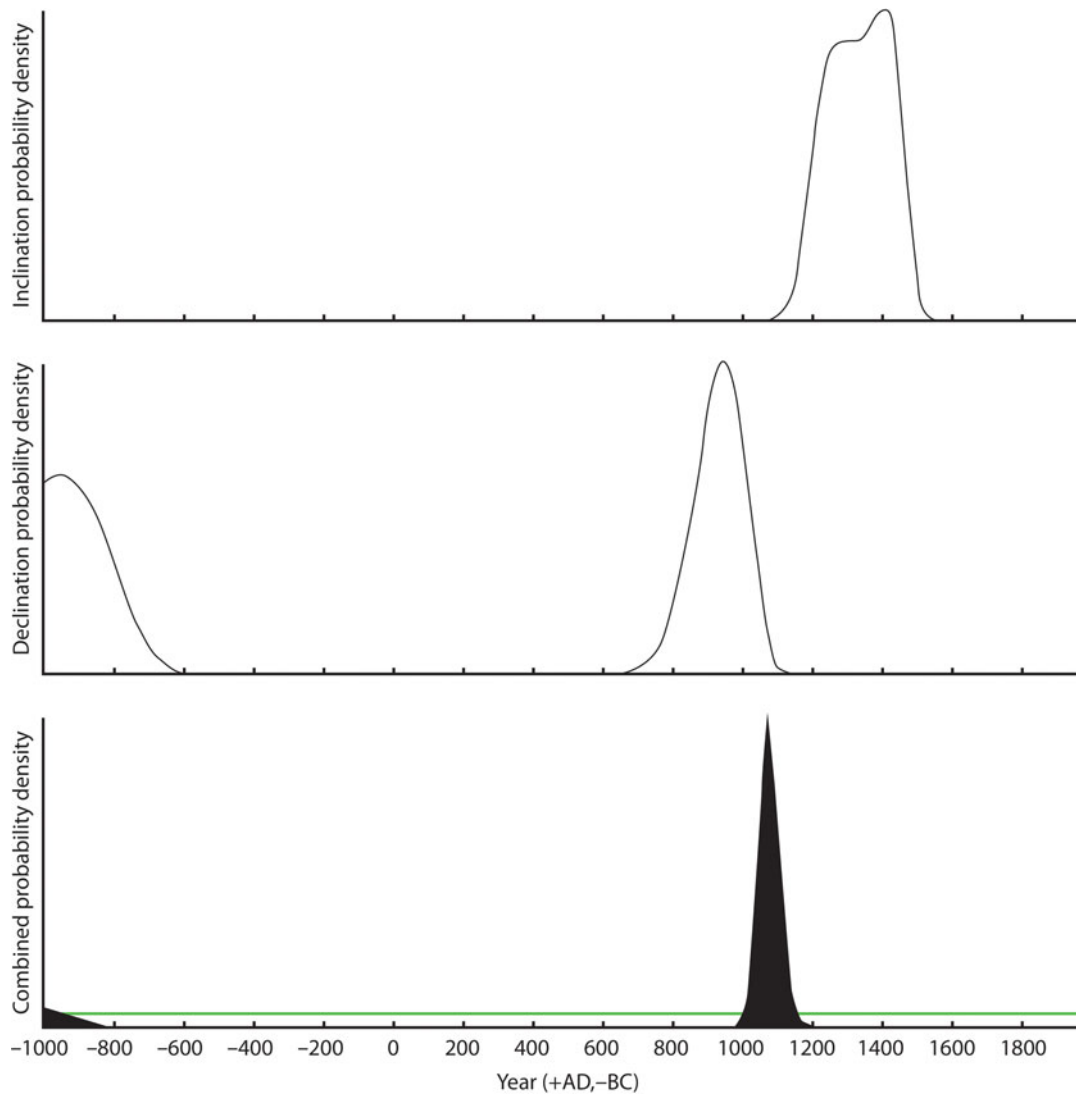


Fig. 4 Calibration of a mean archaeomagnetic direction in the UK using RenDate (Lanos et al. 2005; Zananiri et al. 2007). The upper graph shows dates when the geomagnetic field had the same inclination as the measured direction; the middle graph shows dates when the declinations were the same. The lower graph shows the combined probability density where the geomagnetic field displayed the same declination and inclination as that recorded by the samples. The black area represents the date range with a 95 % confidence interval, in this case either before 950 BC or AD 1000–1160. Additional evidence is required to select from the two possibilities

et al. 1988). Subsequent developments in the data available and statistical approaches have led to better quantification of errors in both the magnetic direction to be dated and the secular variation record (Batt 1997). This has been followed by the use of Bayesian statistical methods to calculate confidence limits and combine the results for magnetic declination, inclination, and intensity (Lanos et al. 1999; Lanos 2004). New modeling techniques allow the consideration of data over larger regions, reducing the need for regionally specific calibration curves (Korte and Holme 2003). For example, Pavón-Carrasco et al. (2009) used a spherical cap harmonic model to produce a secular variation record for Western Europe. Global models can also be produced (e.g., Korte et al. 2009) using worldwide data, but, at present, these do not have the precision needed for archaeological dating.

Applications

Archaeomagnetic studies have been used to investigate a wide variety of archaeological features. Particularly notable case studies include the dating of medieval and Tudor glassmaking furnaces at Bagot's Park, UK (Linford and Welch 2004), brick kilns (Casas et al. 2007), pottery kilns (Reinders et al. 1999), ovens (Schnepp et al. 2003), and canal sediments (Eighmy and Howard 1991). The precision of archaeomagnetic dates is crucial in their use in addressing archaeological questions. A number of factors will influence this precision: recording of the past field, post-firing or post-depositional disturbance, precision of sampling and laboratory measurements, precision of the secular variation record and the method of comparison, and spatial variation of the geomagnetic field. Of these, the most significant is usually the precision of the secular variation curve, and, as this varies with time, the precision of the date obtained will depend on the archaeological period. As the geomagnetic field has occasionally had the same direction at different times, it is also possible to obtain two or more alternative dates for a single archaeological event. In most cases, the archaeological evidence will indicate the most likely. Given the number of contributing factors, it is not possible to define the general precision of archaeomagnetic dates, but there will usually be an error margin of at least ± 50 years (Linford 2006). It is important to note that the secular variation record improves as more measurements become available; hence, features that cannot be dated or give broad age ranges now may be datable in the future.

Considerable research effort has been focused on building up secular variation records, making archaeomagnetic dating a routine dating tool for some archaeological periods and regions. This includes large parts of Europe, most notably Bulgaria (Kovacheva et al. 2009), the UK (Zananiri et al. 2007), France (Gallet et al. 2002), Germany (Schnepp and Lanos 2005), Iberia (Gómez-Paccard et al. 2006), Greece (Tema and Kondopoulou 2011), and Hungary (Marton and Ferencz 2006). There have also been major studies in the American Southwest, where independent dates are provided by dendrochronology (Sternberg and McGuire 1990; Doyel and Eighmy 1994). Work is progressing in other regions, for example, North Africa (Gómez-Paccard et al. 2012), New Zealand (Stark et al. 2010), and Syria (Speranza et al. 2006).

Longer-term changes in the geomagnetic field include magnetic reversals (Merrill et al. 1998, p. 163), and these major changes can be used to date early hominid sites, if they are recorded in associated sediments (e.g., Parés and Pérez-Gonzalez 1995). In addition, archaeomagnetic studies have been used in estimating firing temperatures (Linford and Platzman 2004) and firing duration (Meng and Noel 1989) and in provenancing studies (Rasmussen 2001; Williams-Thorpe et al. 1996). Wider applications are discussed more fully in Sternberg (2001) and Tarling (1983, p. 157).

Conclusions and Future Directions

Archaeomagnetic dating has been shown to provide valuable archaeological information and supplement the suite of chronological tools available for interpreting archaeological sites. In addition, the development of archaeomagnetic dating as a method contributes to the wider understanding of the Earth's magnetic field (Gallet et al. 2009). As noted by Sternberg (2001), archaeomagnetic dating is most effective as a collaborative venture between archaeologists and geophysicists. Independently dated features from an archaeological excavation can provide geomagnetic field information; once the secular variation pattern is established, it can be used to provide archaeomagnetic dates.

Key to improving the accuracy and reliability of archaeomagnetic dates is the availability of magnetic measurements on dated archaeological material. Collaborative sampling ventures such as AARCH (Archaeomagnetic Applications for the Rescue of Cultural Heritage, http://dourbes.meteo.be/aarch.net/frameset_en.html) have increased the data collected, and they are made widely available through international databases, for example, MagIC (Magnetics Information Consortium, <http://earthref.org/MAGIC/>). In many regions, there has been a focus on directional rather than intensity methods. However, experimentally innovative methods for recovering and interpreting archaeointensity (e.g., Gallet et al. 2009; Casas et al 2005) have led to an increased focus on intensity studies, which permit the full magnetic vector to be used in dating studies, thus improving the precision of dates, and allowing the dating of unorientated material.

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Amino Acid Racemization, Eolianites

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Definition

Occurring along many of the world's coastlines, eolianites are geographically extensive, wind-blown accumulations of skeletal carbonate sands derived from the physical breakdown of marine invertebrates from adjacent continental shelves. Eolianite successions have been of interest as archives of long-term environmental change and their potential for reconstructing Quaternary relative sea-level histories. Amino acid racemization (AAR) has been applied to the dating of eolianite successions ("whole-rock" dating) and has involved assessments of relative age, stratigraphical correlation, and, in more ideal situations, the derivation of numerical ages for eolianite units. Fossil molluscs from interstratified shelly facies have also been dated using AAR to constrain the timing of eolianite deposition.

Introduction

Eolianites are stacked, sheet-like deposits of skeletal carbonate sand that crop out along many of the world's coastlines (Fig. 1). The bioclastic sediment comprising eolianite is generated in highly productive inner continental shelf environments, and the sediment is entrained landwards by waves, shallow water currents, and eolian processes. Eolianite sediment typically comprises sand-sized (0.063–2 mm) fragments of skeletal carbonate derived from the physical breakdown of marine invertebrates such as molluscs, echinoids, bryozoans, corals, and coralline algae. Foraminifers and sponge spicules are also commonly present. The term eolianite was introduced by Sayles (1931) in his report on the carbonate dune successions of Bermuda. Non-carbonate minerals may include quartz and heavy minerals. Eolianites have also been described using the lithological term *calcarenite* to avoid the genetic definition, as many facies within these successions were deposited by subaqueous processes. Although by definition, calcarenites contain ≥ 50 % calcium carbonate as framework grains and cement, some eolianites have been noted to have as little as 10 % by mass of calcium carbonate (Murray-Wallace et al. 2001). Eolianite successions represent shore-parallel, composite ancient dune forms which flank many of the world's coastlines. They have been described from coastlines in tropical and temperate regions, and particularly well-described successions occur in the Bahamas, Bermuda, Hawaii, western India, Mediterranean, South Africa, and southern Australia (McKee and Ward 1983; Fairbridge 1995; Vacher and Quinn 1997; Brooke 2001; Bateman et al. 2004; Hearty and O'Leary 2008). Australian eolianite successions extend from Shark Bay, Western Australia, to western Victoria and represent the world's largest eolianite province.

The origin of eolianites has been of global controversy in view of conflicting observations of the field relationships of these deposits (Fairbridge 1995). Along some coastlines eolianites have clearly formed at times of interglacial high sea levels analogous to the present Holocene

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Fig. 1 Eolianite of Robe Range near the town of Robe, in southern South Australia. Robe Range is a composite barrier structure comprising skeletal carbonate sand units of the late Pleistocene warm interstadials MIS 5c and MIS 5a and capped by unconsolidated but vegetated Holocene dune sand. At this site the tabular cross-bedded sands are separated by weakly developed paleosol. The uppermost unit is capped by a pervasive and strongly indurated calcrete. A person stands as scale at the crest of the structure. The cliff is approximately 20 m high

interglacial such as the Coorong Coastal Plain in southern Australia (Sprigg 1952; Murray-Wallace et al. 1998). This has been confirmed by dating using a variety of geochronological methods, the results of which correlate with sea-level highstands of the past 300,000 years for many of the world's coastlines (Vacher and Quinn 1997). On the Coorong Coastal Plain in southern Australia, the eolianite record extends back in time over 1 Ma (Murray-Wallace et al. 2001). Other coastlines, however, indicate eolianite formation at times of lower sea level during glacials *sensu lato* in addition to deposition during interglacials such as parts of the Hawaiian Islands (Stearns 1985) and the Swan Coastal Plain, near Perth in Western Australia (Price et al. 2001). During such intervals, global ice volumes were larger and sea levels were lower than present. In these situations, eolianites formed in response to stronger onshore winds carrying sand-sized skeletal carbonate fragments landwards from the partially, or completely, subaerially exposed continental shelves. The calcium carbonate was formed at times of higher sea level, and the subsequent landward migration of the carbonate sediment occurred by eolian processes following a fall in sea level (forced regression) or wave, shallow water currents, and eolian activity accompanying a relative rise in sea level (transgressive-related sedimentation). The outer surfaces of the dune accumulations were then consolidated by vegetation cover and soil development. Further evidence for the glacial age (*sensu lato*) of some eolianite successions is that the basal units extend below present sea level implying a lower sea level at the time of their formation and scuba diving has identified erosional shoreline notches within dune limestones that also formed at times of lower sea level (Stearns 1985).

Numerous sedimentary structures are preserved within eolianites from which inferences about relative sea level may be derived (McKee and Ward 1983). Eolian trough cross-bedding and other sedimentary structures (e.g., topset, foreset, bottomset, grain avalanche structures, trace fossils such as animal footprints) represent relational sea-level indicators, having clearly formed above tidal datum (Fig. 1). In settings where active eolian dunes have migrated into standing bodies of water such as coastal lagoons, however, it may be possible to infer relative sea level, albeit crudely, based on the presence of distinctive fossils and interfingering relationships with lagoonal muds.

Eolianite “Whole-Rock” Dating

Despite advances in geochronological methods, it remains a difficult task to establish the age of many Quaternary sedimentary successions and landforms. In many field contexts, requisite mineral phases may be absent (e.g., fossil corals for U-series dating), or the relevant assumptions of geochronological methods are not upheld. AAR has been applied in the dating of eolianites, particularly in contexts where quartz sand is not available for luminescence dating or where entire fossils and other mineralogical constituent are absent that would otherwise have been suitable for dating by other methods (Milnes et al. 1987; Kimber et al. 1994; Kindler and Hearty 1997; Hearty et al. 1992; Hearty 1998; Brooke et al. 2003; Murray-Wallace et al. 2001, 2010). AAR has been applied to dating eolianite successions as the method is applicable to a substantial portion of the Quaternary timescale. Technological advances in the detection limits of amino acid residues in fossils (e.g., reverse-phase, high-performance liquid chromatography) have now made it possible to analyze individual microfossil components from eolianites (e.g., foraminifers such as *Elphidium* sp.).

As with all AAR-based chronologies, the age range of the whole-rock method is a function of diagenetic temperature. Lower latitude sites, characterized by higher current mean annual temperatures, will have experienced higher diagenetic temperatures. Accordingly, the age range of the technique is spatially variable and will be less in lower latitudes than for higher-latitude regions with lower diagenetic temperature histories. Based on a regional study of isoleucine epimerization of eolianite in the Bahamas (current mean annual temperature 23–25 °C), Hearty and Kaufman (2000) concluded that the method is applicable to the past 450–500 ka (i.e., back to about MIS 13). Whole-rock analyses from the Coorong Coastal Plain in southern Australia (CMAT 14.7 °C) have yielded a leucine D/L value of 0.843 for eolianite from the East Naracoorte Range, which based on magnetostratigraphy is regarded as older than 780 ka, and therefore indicating that in this region the practical limit of the AAR method is approximately 1 Ma (Murray-Wallace et al. 2001).

Whole-rock dating is based on the notion that sedimentary particles, if sufficiently well preserved, may be directly dated by AAR and reliably indicates the age of the sedimentary deposit. This is potentially the most complicated application of AAR as considerable background information is required for each field site. Similarly, the results from one field area cannot be assumed to directly apply to another, even within a restricted geographical area. For example, the residence time of sedimentary particles (i.e., time lag between skeletal carbonate formation and their final incorporation within a geological deposit) needs to be quantified for each sedimentary environment. This commonly involves the analyses of modern beach sand, sampled from beach surfaces (e.g., upper 2 cm of sand). Quantification of the residence time may be achieved through calibration by an independent dating method such as radiocarbon dating on a subset of framework grains, but the value determined remains unique to that environment and local field setting.

Dating Eolianites: Analytical Methods

Coarse-grained skeletal carbonate sand (bioclasts) from eolianite is most suited to the whole-rock method (Hearty 1998; Murray-Wallace et al. 2001) as the pretreatment strategies are easier with larger bioclasts (e.g., HCl digestion of outer carbonate grain surfaces). Typically, such sedimentary particles are represented by comminuted molluscs, foraminifers, bryozoans, echinoids, and corals.

An important requirement for whole-rock dating is that the sediment has been rapidly buried and not subjected to prolonged intervals of subaerial exposure, thus significantly reducing uncertainties

about racemization rates and diagenetic temperatures. Shallowly buried sediment (< 1 m) will be characterized by disproportionately high D/L values, a function of the exponential effect of higher, summer temperatures on diagenetic racemization. Accordingly, rapid, deep burial largely removes sediment from the influences of weathering, pedogenic processes, erosion, and subaerial exposure, ensuring that the sediment sampled has remained buried since deposition and is more likely to be better preserved. Collection of whole-rock samples from depths greater than 1 m will ensure that the diagenetic temperature history reflects temperature changes associated with long-term climate changes, rather than seasonal temperature variations. The extent of racemization in whole-rock samples will accordingly represent the integrated kinetic effect of racemization in each of the fossil fragments. Commonly, the most reliable approach for sediment sampling is to auger into the face of an outcrop (natural rock face or quarry exposure) ensuring that the location of the sediment sample is at least 1 m below the natural ground surface. It is also critical from the perspective of diagenetic temperature histories to note the relation of the sediment sample to any subaerial exposure surfaces such as calcrete horizons within the sedimentary succession. Settings subjected to regular alternate wetting and drying should be avoided such as outcrops within the intertidal zone as they are likely to have been subjected to prolonged leaching and diffusive loss of amino acids, particularly in terms of amino acids bound within lower molecular weight peptides and free amino acids. Such contexts also commonly show the effects of reprecipitation of calcium carbonate.

Eolianite sample preparation initially involves the physical disaggregation of sediment to remove any carbonate cement adhering to sediment grain surfaces. Removal of cement involves cleaning in distilled water in an ultrasonic bath followed by an H_2O_2 rinse to remove organic compounds and followed by a dilute acid (HCl) etch to remove any additional cement and the outer portion of sediment grains. The mineralogical integrity of the framework grains can be examined in part through microscopy and X-ray diffraction analysis of an aliquot of the whole-rock sample. Commonly, a subset of sediment grains for AAR analysis are selected through sieving sediment (e.g., particle sizes 250–850 μm ; Hearty 1998; 63–500 μm ; Murray-Wallace et al. 2001). Analyses have commonly been undertaken on the total hydrolyzable amino acids of the intercrystalline fraction, and it is advisable to analyze free amino acids from the same sample before undertaking acid hydrolysis, as an additional means of evaluating integrity of results. Given the complexities of whole-rock dating, analyses of the intracrystalline fraction would also be advisable following the analytical protocol set out in Penckman et al. (2008). More recently the analysis of single foraminifers such as the genus *Elphidium* sp. has greatly enhanced the dating of eolianite (Lachlan 2012) using reverse-phase, high-performance liquid chromatography (RP-HPLC) (Kaufman and Manley 1998).

Complexities in Eolianite Dating

The dating of eolianite is most effective in field settings in which cyclic sedimentation has produced the successions, such as successive interglacials. In these contexts, sufficient time has elapsed between the deposition of different sedimentary units, for them to be statistically resolved based on extent of AAR. A related advantage is that in the most general sense, sedimentary successions of different interglacials may have experienced similar changes in diagenetic temperatures over multiple glacial cycles.

AAR whole-rock sample preparation should also involve the physical removal of strongly abraded and etched grains from the sample population of grains before HCl digestion. The reworking of older sedimentary particles into younger sediments potentially complicates the

application of AAR to whole-rock dating, particularly if the proportion of reworked framework grains is not quantified. Older grains will be characterized by higher D/L values provided that the grains have not lost amino acids through in situ leaching (diffusive loss of free amino acids and amino acids bound in lower molecular weight peptides). The magnitude of reworking of older skeletal carbonate grains into modern sediment will reflect the sediment dynamics of individual study sites and will be a function of local carbonate bioproductivity in the formation of modern carbonate grains and the rate of input of older carbonate grains from the erosion and reworking of Holocene or Pleistocene sedimentary units. In southern Australia, modern beach sediments have yielded high D/L values indicating a significant input of relict carbonate grains from locally outcropping Pleistocene eolianite successions (Murray-Wallace et al. 2001, 2010). At Parsons Beach on Fleurieu Peninsula, South Australia, for example, modern beach sand collected from the uppermost 2 cm of a beach face yielded D/L values of 0.253 for glutamic acid and 0.189 for valine (total hydrolyzable amino acids measured by HPLC) compared with 0.614 and 0.545, respectively, from a last interglacial eolianite succession at Knight Beach on Fleurieu Peninsula (Murray-Wallace et al. 2010). Modern marine molluscs (alive at the time of collection or recently dead) consistently yield low D/L values in the range of 0.02–0.03 for valine and glutamic acid, respectively, further highlighting the magnitude of sediment reworking in the Parsons Beach example. At Long Beach, Guichen Bay near Robe in southern Australia, modern beach sediment yielded a D/L value of 0.225 for leucine (total hydrolyzable amino acids by gas chromatography) and 0.679 for free amino acids (Murray-Wallace et al. 2001). A last interglacial eolianite from a coastal barrier termed Woakwine I (132 ± 6 ka) yielded a mean leucine D/L value of 0.451 ± 0.099 .

Aminostratigraphy

AAR has most commonly been applied to the dating of eolianites in the context of *aminostratigraphy* (Miller and Hare 1980). Aminostratigraphy involves the classification of strata into chronostratigraphical units or *aminozones* that correspond with intervals of time, termed geochronological units (Salvador 1994). Litho-, bio-, and morphostratigraphical evidence is generally used to support these chronostratigraphically defined units, as well as calibration by other geochronological methods. The fundamental unit of aminostratigraphy, the *aminozone*, refers to a single time-stratigraphical unit representing a well-defined interval of time (e.g., single stages of the marine oxygen isotope record) and is delineated by the clustering of amino acid enantiomeric values on replicate fossils from a single, mappable lithostratigraphical unit. According to Miller and Hare (1980), this approach involves the least ambiguous application of AAR data, as it largely overcomes the uncertainties associated with racemization kinetic models and diagenetic temperature histories. Traditional practice has seen the application of this tool in restricted geographical settings to overcome regional uncertainties in diagenetic temperature histories.

By far the majority of applications of AAR have involved stratigraphical correlation and assessments of relative age. The earliest attempts at assessing age equivalence of disjunct sedimentary successions tended only to be undertaken within restricted geographical regions, so that the assumption was upheld that different sedimentary deposits of presumed equivalent age had experienced similar diagenetic temperatures.

Selected Case Studies

One of the first examples of AAR “whole-rock” dating was reported on the extent of racemization of aspartic acid, alanine, leucine, and valine (total hydrolyzable amino acids) in carbonate sediment from a 3 m profile at Piednippie Hall in South Australia (Milnes et al. 1987). Their results revealed a monotonic increase in the extent of racemization down profile with the most promising results for the fast racemizing acid, alanine. Since this early reconnaissance study, whole-rock dating of eolianite has represented a valuable application of AAR in studying Quaternary coastal carbonate successions (Hearty 1998; Murray-Wallace et al. 2001). In a comprehensive study of the geology of Eleuthera Island, Bahamas, Hearty (1998) used the degree of isoleucine epimerization in skeletal carbonate sands as a method for discriminating eolianites of contrasting age. Sediments from eolian dune, beach, and wash-over facies revealed a generally high level of concordance for replicate samples, suggesting that the “whole-rock” method may yield reliable geochronological information for Quaternary morphostratigraphical studies. For example, twelve analyses on a minor paleosol developed on beach and eolian sediments yielded a mean D/L value for isoleucine of 0.379 ± 0.027 (Hearty 1998). The coefficient of variation for these data of 7.12 % compares favorably with results typically obtained on fossil molluscs from a single deposit (Murray-Wallace 1995). Thus, although the age of lithoskels comprising skeletal carbonate sands may be potentially of contrasting ages, the overall averaging effect in well-sorted sand may yield a high level of reproducibility in replicate analyses. Using the whole-rock method, Hearty (1998) was able to discriminate interglacial deposits on Eleuthera Island correlating with MIS 1, 5a, 5c, 7, 9/11, and ≥ 13 .

The whole-rock method has also been applied to a succession of eolianite coastal barriers of the Coorong Coastal Plain in southern Australia (Murray-Wallace et al. 2001). Up to thirteen well-defined barriers occur across the 90 km coastal plain associated with deposition during interglacial sea-level highstands since the onset of the middle Pleistocene (Murray-Wallace et al. 2001). The ages of the barriers had previously been determined on the basis of luminescence dating (Huntley et al. 1993, 1994). Samples for whole-rock dating were obtained from the same stratigraphical units studied by Huntley et al. (1993, 1994). The extent of leucine racemization (total hydrolyzable amino acids and free amino acids) in the Pleistocene skeletal carbonate sand (63–500 μm) increases monotonically with age and is consistently higher than for entire fossil molluscs from the same stratigraphical units, reflecting the lengthy residence time for bioclasts within the study area (Murray-Wallace et al. 2001). The extent of racemization in the whole-rock samples conforms to a model of apparent parabolic kinetics, and the numerical ages determined on the basis of degree of leucine racemization were generally in accord with the luminescence ages reported by Huntley et al. (1993, 1994). The oldest amino acid racemization-derived age of 935 ± 178 ka was for eolianite from the East Naracoorte Range, which is known to predate the Brunhes-Matuyama boundary (> 780 ka).

Summary and Conclusions

Amino acid racemization has been applied in establishing geochronological frameworks for eolianite formation for a range of Quaternary coastal successions from around the world. The principal advantages of applying AAR to the dating of eolianites include the ability to derive relative ages significantly beyond the range of radiocarbon methods (> 50 ka) and, for some coastal regions, significantly beyond the range of U/Th or traditional methods of luminescence

dating and accordingly resolve the ages of several interglacials. With refinements in chromatographic detection of amino acids such as reverse-phase, high-performance liquid chromatography, it is now possible to analyze individual carbonate grains or foraminifers and examine the dynamics of sedimentary environments (e.g., quantify the magnitude of reworking of sedimentary particles). The analysis of eolianites by AAR is a far from trivial task and the “black box” approach to analysis should be avoided.

Cross-References

- ▶ [Amino Acid](#)
- ▶ [Amino Acid Racemization, Coastal Sediments](#)
- ▶ [Amino Acid Racemization, Marine Sediments](#)
- ▶ [Amino Acid Racemization, Palaeoclimate](#)

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Luminescence, Flints and Stones

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Introduction

Most applications of luminescence dating of flints and stones are related to archaeology and the timing of prehistoric sites. Here, prehistoric human activities are directly dated in most cases, using the last heating of flint, chert, limestone, quartzite, or quartz. This is in contrast to surface exposure dating of such materials, where the event dated – the last exposure or burial – is often not related to the event of the human occupation or activities. Consideration of the relation between the event dated and the research question asked (i.e., sedimentology, human activity, etc.) is crucial. This is well discussed in Dean (1978), who describes a “typology of events.” Luminescence dating is especially useful in archaeological context at the limits or beyond the range of radiocarbon dating of organic material or when the latter is lacking (see “► [Luminescence Dating](#)”). The time span of application ranges from a few to several hundred ka. However, recent developments employing orange-red TL (Richter 2011) suggest applicability close to 1 Ma under favorable circumstances.

Thermoluminescence (see “► [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)”) is often employed for determining the heat exposure age, but in principle, optically stimulated luminescence (OSL, see “► [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence Cosmogenic Nuclides](#)”) can be employed as well. However, OSL is not generally applicable to materials classed as flint, obsidian, etc., and therefore, only few studies investigate such theoretical venues (Schmidt and Kreutzer 2013; Poolton et al. 1995; Polymeris et al. 2010). Rock material without significant amorphous phases, i.e., containing significant amounts of α -quartz (see “► [Quartz](#)”) such as unheated quartz pebbles, is also suitable for surface exposure dating (see “► [Luminescence, Rock Surfaces](#)”). Here, the time of the last exposure to light is dated (e.g., Sohbaty et al. 2012; Kouremenos 2008) which is not necessarily a prehistoric human activity, such as turning rocks over (e.g., Greulich and Wagner 2009).

Luminescence of Heated Flint and Stone

The principles of dosimetric dating (see “► [Luminescence Dating](#)”) and associated physical phenomena (see “► [Radiation and Radioactivity](#)”) apply. The radiation dose, as determined by luminescence methods, is caused by ionizing radiation from within the sample as well as its surroundings. The ratio of radiation dose (palaeodose, P) to dose rate ($\dot{D}$) provides the age. Archaeological flint and stones (luminescence properties) as well as their context (dosimetry) exhibit some specific aspects which are different from other applications of such methods, such as ESR or optical dating (Richter 2007).

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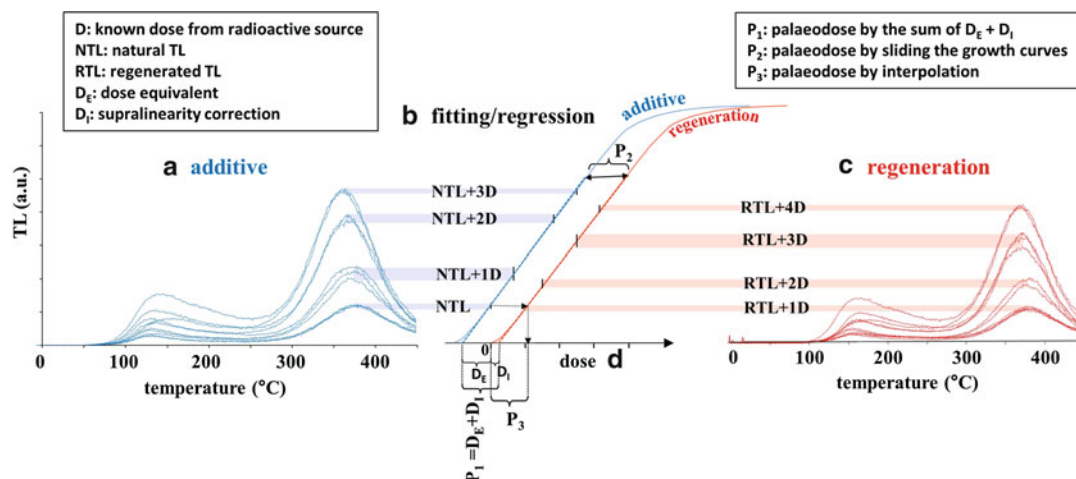


Fig. 1 Three different methods for estimating palaeodoses (P_1 , P_2 , P_3) (a) additive TL signals in blue, where NTL is the natural TL signal and NTL+D is the natural TL plus the TL induced by additional artificial irradiation; (b) solid lines show the theoretical signal growth with dose (d) of the additive (light blue) and regeneration dose growth curves (light red), both exhibiting supralinear behavior. Dotted lines show fitted data (plotted as peak heights) with regression analysis respectively. (c) Regeneration TL signals in red, where RTL+D is the TL from artificial irradiation after having heated the sample. The sum of the regression (dotted blue) of the additive growth curve (dotted blue line providing the equivalent dose, D_e) and the regeneration growth curve (dotted red line providing the supralinearity correction, D_s) are giving the total absorbed dose (palaeodose, P_1) in a multiple-aliquot additive regeneration (MAAR) protocol. Shifting of either growth curve (slide) along the x-axis (dose) provides P as well (P_2), while interpolation of the natural signal on the regenerated dose growth curve determines P in a single-aliquot regeneration (SAR) protocol (P_3)

Samples and Sample Selection

Samples are primarily selected on the basis of suitability for dating. In the case of heated material, macroscopic features like crenation, reddening, craquelation, potlids, etc., are strong, but not conclusive (e.g., Richter 2007) indicators of heat alteration of lithic material. In most contexts, natural fires can be excluded as cause of the heating (Richter 2007; Alpersen-Afil et al. 2007); however, the time difference between anthropogenic and natural firing is likely not significant in most circumstances (Richter and Krbetschek 2014a). The sufficiency of the prehistoric zeroing for dating application can be tested for by using the material's luminescence properties, such as the presence of a heating plateau and an equivalent dose plateau (Aitken 1985). Sample size requirements depend on the technique/protocol used to evaluate the palaeodose (see below). In any case, the outer 2 mm of samples are sawn off in order to exclude those parts which have received a radiation dose from α -/ β -radiation originating from outside the sample. Thus, the number of parameters in age calculation is reduced and precision is increased. However, this requires minimum sample thicknesses of 5–6 mm, and thus several grams of weight, mostly dependent on sample shape. For standard techniques based on multiple aliquots, about 1 g of material has to remain after the removal of the outer 2 mm, but much less is required for single-aliquot procedures (Richter 2011).

For optical dating of surfaces of rocks, the outer 2 mm surface area is not to be removed because of limitations in the bleaching depth of the light causing the zeroing of the signal.

Palaeodose Determination

The thermoluminescence (TL) signal of most heated flint and stone samples exhibit (significant for flint) supralinear growth of the TL signal with dose/age (Fig. 1). This behavior is also seen in inclusion pottery dating (see “► Luminescence, Pottery and Bricks”; Aitken 1985). In the standard application of the technique, several groups of multiple aliquots (subsamples) receive a suite of

irradiations from a calibrated ionizing source (see “► [Radiation and Radioactivity](#)”). While the dose producing the natural signal (palaeodose, P , or equivalent dose, D_E) is not known, increasing the luminescence signal by several artificial irradiation steps of known dose (dose points) provides the sensitivity (slope of luminescence versus dose) of each individual sample to ionizing radiation. Regression analysis of the measured luminescence signals that are given artificial doses (additive dose growth curve in Fig. 1) provides an equivalent dose (D_E) in the multiple-aliquot additive dose (MAAD or MAD) protocol. The supralinear growth of the signal at low doses is considered by a second regression (supralinearity correction, D_I) of luminescence signals from aliquots which were zeroed in the laboratory prior to irradiation (regeneration dose growth curve). In this multiple-aliquot-additive-regeneration (MAAR) protocol, the sum of D_E and D_I provides the total absorbed dose (palaeodose, P) the sample has received since its zeroing in antiquity (Aitken 1985). Extrapolation procedures for large palaeodoses when the natural luminescence signal is at the onset of saturation, however, are prone to error and not precise. In such cases, the palaeodose can be determined by sliding one of the two dose growth curves along the dose axis until they match (Fig. 1) and the absolute value of the slide provides the palaeodose (e.g. Mercier et al. 2004). In single-aliquot regeneration (SAR) techniques, the natural luminescence signal is just interpolated on a regenerated dose growth curve (Fig. 1) (Richter and Krbetschek 2014b). So far this technique appears to be restricted to heated flint using the orange-red thermoluminescence (Richter and Krbetschek 2006; Richter and Temming 2006) and has not been applied regularly. However, it allows the dating of rather small samples (Richter 2011), which is also possible in OSL techniques (see “► [Luminescence Dating](#)”) which are commonly based on a SAR protocol, as well as for dating heated materials or in surface exposure dating.

Dosimetry

The dosimetry (see “► [Luminescence Dating, Dose Rate](#)”) in luminescence dating of flints and stones can be grouped into internal and external dose rates. The former stems from the content in radionuclides of the sample (commonly U, Th, K) and is determined by geochemical analysis (e.g., see “► [Neutron Activation Analysis](#)”). A common value for the sensitivity of the sample to α -radiation (a- or b-value) is often assumed for quartz pebbles (in addition to the assumption of a small internal dose rate) but should be individually determined for at least the majority of samples especially in heated rock TL dating, because of large variability even within supposed single sources of the origin of the material (especially flint). Recent analysis has shown that significant variation is exclusively correlated to macroscopic visible differences in flint (Schmidt et al. 2013), which is the most commonly employed material. These visible differences include veins, inclusions, etc., which have to be removed in any case, because they obviously belong to different mineral phases. The luminescence properties of different phases are likely to be rather different, and such composite signals cannot, a priori, provide accurate results. Therefore, with the removal of such phases, and other geochemically instable parts like patination, the assumption of insignificant variability is valid, and the internal dose rate can be considered as stable over the entire time range of the method.

The external dose rate originates from outside the sample, i.e., radionuclides contained in the surrounding matrix (sediment, éboulis, gravel, blocks of stone, cave walls, lithics, bones, etc.) and a cosmic contribution. Surprisingly in most cases the assumption of constancy of the external dose rate (see “► [Luminescence Dating, Dose Rate](#)”) appears to be valid but should always be verified by laboratory gamma spectrometry to the extent possible. In heated rock dating, the contribution from external α -/ β -radiation does not have to be considered because of the removal of the outer 2 mm. While these could be modeled, the complex shapes of especially artifacts would presumably result in low-accuracy age determinations. The, usually small, cosmic dose rate depends on depth of burial,

altitude, and latitude and is considered as stable. The external γ -dose rate often dominates the total dose rate, and ages are thus very dependent on the accurate determination of this parameter (see Richter 2007; Table 1 for a hypothetical example). Because samples are almost always removed from context prior to dosimetric analysis, the external γ -dose rate cannot be measured at the exact location of the samples. If sediments are heterogeneous (e.g., in caves), analogous locations of geometries similar to the sample positions are required for in situ measurements by portable γ -spectrometry or dosimeters in 30 cm deep holes ($4\text{-}\pi$ geometry). Alternatively, each excavated surface ($2\text{-}\pi$ geometry) can be measured with portable instruments (Guérin and Mercier 2012). A discussion on the implications of the external dosimetry and methods used can be found in Richter (2007); and Richter et al. (2014). Because the external γ -dose rates cannot be determined at the find spot, it is advisable to approach the age of a lithic assemblage by measuring multiple samples and employ an average external dosimetry from several readings (Richter 2007). This often results in large uncertainties associated with this parameter and consequently large uncertainties in individual ages. Such derived average external dose rates do not necessarily correspond to the dose rate the sample actually was exposed to during burial, and the resulting individual TL ages may be too young or too old. This results in large spreads of TL ages for a given context, and the individual sample ages have to be interpreted with caution. However, this can be overcome by dating multiple samples from a context, yielding an average TL age derived from all samples. This provides a good representation of the context age (e.g., Richter and Krbetschek 2014a). Obviously, averaging requires strong indications of the validity of the assumption that the heating of samples took place roughly at the same time. Alternatively, the external γ -dose rate can be modeled, and the dosimetry estimated for single samples (Guibert et al. 1998; Guérin 2012), provided that the heterogeneity of the sediments is extremely well documented. In general the confidence in TL-dating results of heated flint depends on the ratio of internal to external dose rate, where samples with large internal (stable) dose rates are considered more reliable than others (Richter 2007).

Application of Luminescence Dating of Flint or Stone

Luminescence dating of heated flint and stone is playing a major role in establishing chronostratigraphies, e.g., for the expansion of humans out of Africa or the settlement of Europe. TL dating of heated flint established the quasi contemporaneity of early modern humans at Skhul (Mercier et al. 1993) and Qafzeh (Valladas et al. 1988) at >100 ka and with Neanderthals (Valladas et al. 1987) at about 60 ka in the Levant. These studies showed for the first time a potential time period for these species to meet; however, actual evidence of such is still missing. The antiquity of elaborate figurative art of ca. 40 ka was shown by standard TL protocols for heated flint by Richter et al. (2000) for the site of Geißenklösterle cave in Southern Germany. This site yields some of the most intriguing examples of the Upper Paleolithic art, with figurines made from ivory depicting animals as well as humans. TL-dating results agreed only with some of the available radiocarbon data, the latter of which showed a variability considered as inconsistent with site formation. However, it was not until the improvement of pretreatment methods of radiocarbon dating of bone until excellent agreement was shown between ^{14}C and TL (Higham et al. 2012). While these samples had their natural TL well within the linear dose range of heated flint, artifacts from Menez-Dregan I (France) could only be dated by the slide method, due to their antiquity of ca. 200 ka (Mercier et al. 2004). Heated flint artifacts from the Middle Paleolithic lake site of Neumark-Nord 2 rarely exceed weights of 5 g, inhibiting the application of standard MAAR regression procedures. The application of a SAR protocol resulted in an Eemian (early last interglacial) age for the last

heating, which is in excellent agreement with stratigraphy, palynology, sediment OSL, and magnetic dating (Sier et al. 2011; Richter and Krbetschek 2014b).

Less frequently used materials sometimes provide specific challenges, especially for dosimetry. The general assumption of homogeneous distribution of radionuclides is not valid in quartzite, and internal microdosimetric modeling is required to determine reliable ages (Tribolo et al. 2006). An age of 74 ± 5 ka was obtained for five burnt lithics of the Still Bay layers at Blombos Cave (South Africa). This result is in good agreement with both ESR dates on teeth and OSL dates on sediment (Tribolo et al. 2006), demonstrating the antiquity of “modern behavior” in Africa. Heated limestone was dated by Roque et al. (2001) for the Upper Paleolithic site of Combe Saunière (France). The problem of spurious TL, usually interpreted as the result of a decarbonation process, was avoided by measuring the TL from the calcite crystals in a carbon dioxide atmosphere. TL dates obtained were found in good agreement with radiocarbon dates.

The last heating of lithic material can be dated by optically stimulated luminescence (OSL) for some materials as well. OSL dating of heated rock sandstone revealed consistent ages around 8 ka for clusters of hearths in the Saharan Fazzan Basin (Libya), which will allow more detailed reconstruction of the Neolithic use of the landscape of this area (Armitage and King 2013). Quartz does not need to be heated for dating purposes, but the event dated is then the last exposure to light, routinely used to determine deposition ages of sediments (see “► [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)”). Excellent agreement was obtained for OSL dating of the outer millimeter of the buried surface of a rockfall boulder with the OSL dating of quartz grains from the underlying sediment, as well as with AMS radiocarbon estimates of a cottonwood leaf found immediately between the clast and the underlying sediment (Chapot et al. 2012), implying a minimum age of 900 years for the creation of the rock art. Application of OSL is by no means limited to archaeological context, and satisfying agreement was obtained for unheated Holocene beach cobbles, from which the buried undersides were dated (Kouremenos 2008).

TL dating of heated flint artifacts has also served to detect site disturbances. A previously unnoticed severe mixing of a Paleolithic site was indicated by the large variability in TL-dating results of heated flint from an assemblage believed to represent a short time span. The age differences of two samples from the same layer with ages of 38 and 5 ka can only be explained by sedimentary disturbance (Debenham 1994). TL dating can further provide indications for the correct attribution of mixed lithic assemblages to technocomplexes. In the case of the Paleolithic site of Chez-Pinaud Jonzac, the TL results for burnt flints from a mixed context provided age estimates in accordance with the result of the lithic analysis, suggesting an Upper as well as a Middle Paleolithic occupation based on diagnostic artifacts (Richter et al. 2013).

Conclusions

Luminescence dating of flint and stone is an important tool, especially in establishing chronologies for the Paleolithic period by determining the age of lithic assemblages through dating the last heating of artifacts. Thermoluminescence dating of heated flint has a major impact in our understanding of the later human evolution, especially the spread of early modern humans and the replacement of Neanderthals. The most useful time range lies beyond the calibration range of radiocarbon dating, because the precision achieved with luminescence methods is often not high enough to answer chronological or chronostratigraphic questions related to Late Upper Pleistocene and later period research. In the light of achievable uncertainties, it always has to be considered if these techniques

actually can provide results capable of answering the question raised. Individual uncertainties in ages at 1- σ between 5 % and 10 %, which is 10–20 % at 95 % probability, can be achieved, and precisions of about 3 % (1- σ) can be obtained for weighted average ages when the same context is dated by multiple samples. Such a precision is comparable to calibrated radiocarbon data at the limits of the ^{14}C method. Dating of objects larger than twice the range of β -radiation includes a stable dose-rate component which increases confidence in age result. The various luminescence techniques employed in dating flint and stone have been shown to agree very well with other dating evidence, while often having the advantage that a human action is directly dated.

Cross-References

- ▶ [Chert](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Luminescence Dating, Uncertainties and Age Range](#)
- ▶ [Luminescence, Pottery and Bricks](#)
- ▶ [Luminescence, Rock Surfaces](#)
- ▶ [Neutron Activation Analysis](#)
- ▶ [Quartz](#)
- ▶ [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Radiation Dose Rate](#)

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Uranium-Lead, Metamorphic Rocks

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Definition: The word metamorphism derives from the Greek word “metamorphosis,” meaning change of form. Metamorphism is the process by which the mineralogy of rocks is changed as the result of pressure and temperature according to their composition and with the aid of fluid and deformation. Metamorphism is mainly concerned with the changes that take place when rocks are in the solid state, even though melt can be one of the phases present.

Introduction

Dating of metamorphism in general aims to determining the absolute age of stages or phases of metamorphism. It requires dating of a mineral or mineral growth zone that reacted or formed during metamorphism. The age is determined by measuring the U–Th–Pb isotopic composition in the mineral (see ► [Uranium-Lead Dating](#)). The crucial step in dating metamorphism is to relate an absolute date to a metamorphic stage or reaction, ideally identified by specific pressure and temperature values. This step is particularly challenging for U–Pb dating as the minerals used are minerals that are typically present in minute amounts within a rock (i.e., accessory), and their behavior and stability during metamorphism are not always well known or easily determined.

Methods

In principle all the analytical techniques used for U–Pb geochronology in other settings can be used for dating metamorphic rocks. Minerals in metamorphic rocks naturally exhibit growth zonation as a result of multistage evolution over a range of conditions throughout their history. While zoned minerals are a powerful tool to reconstruct metamorphic evolutions, the accurate dating of metamorphic stages from the analysis of zoned minerals requires micro-sampling. Microbeam techniques such as ion microprobes (see ► [Secondary Ion Mass Spectrometry: SIMS](#)), laser ablation–inductively coupled plasma mass spectrometry (LA-ICPMS), and electron microprobes (see ► [Chemical Isochron Uranium-Lead: CHIME](#)) are thus most widely used to date metamorphic U–Th minerals. These techniques achieve precise age determination (± 1 % for SIMS and LA-ICPMS) by analyzing small crystal domain (20–50 microns across for SIMS and LA-ICPMS and a few microns for CHIME) in situ, i.e., directly on the polished surface of a crystal.

The identification of the specific growth zones in U–Th minerals is achieved through chemical imaging (Fig. 1). Backscattered electron imaging can be used on all the minerals, but the internal zoning in zircon and baddeleyite is best imaged using cathodoluminescence. Both these imaging

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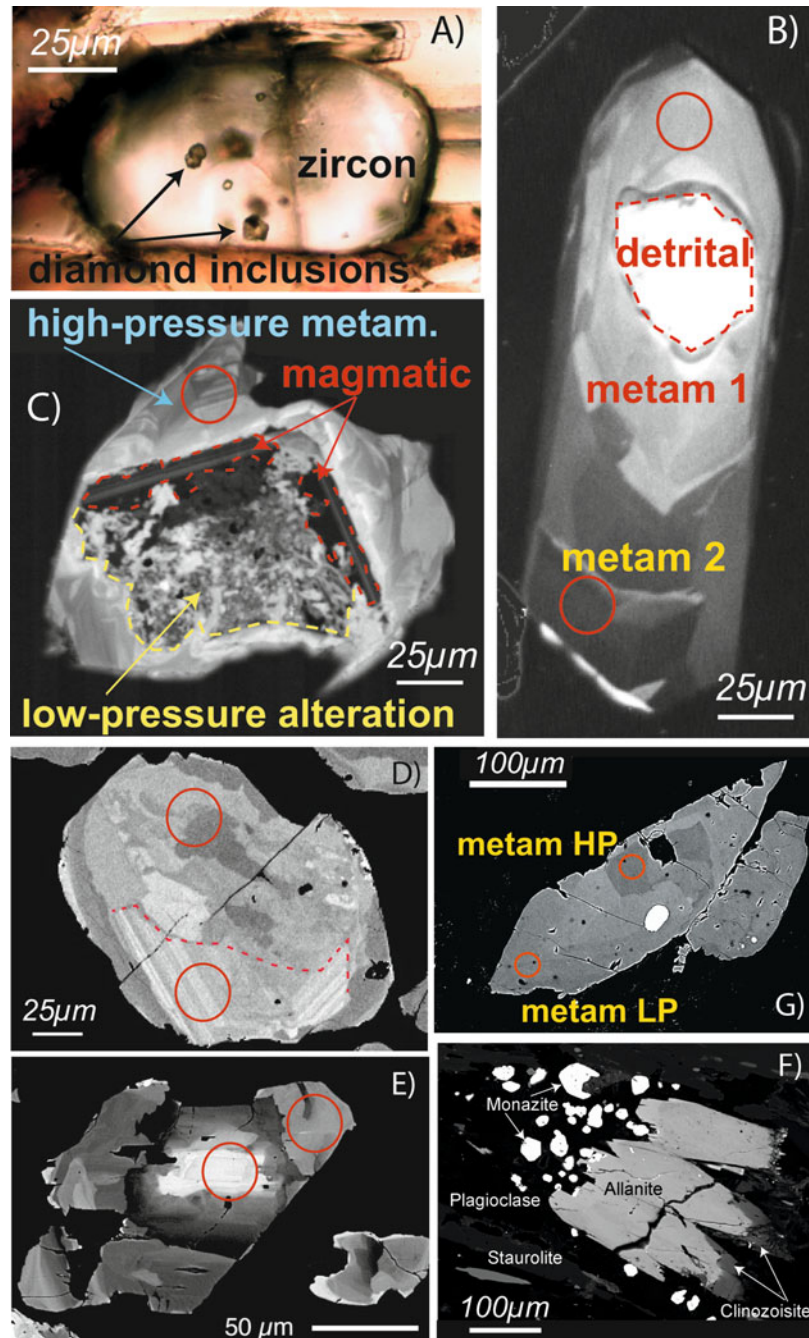


Fig. 1 Images of internal zoning of U–Th minerals from metamorphic (metam) rocks. (a) Light microscope photomicrograph of a zircon with diamond inclusions (Kokchetav UHP gneiss). (c, d) Cathodoluminescence images of zircons. (b) Zircon from a migmatite of the Central Alps that shows two distinct metamorphic overgrowths on a bright detrital core. The metamorphic overgrowths are different in age and both formed during migmatization (Rubatto et al. 2009). (c) Zircon from an eclogite-facies schist from New Caledonia that preserves relicts of the magmatic zircon, domains that record low-temperature alteration at the ocean floor, and high pressure rims formed during subduction (Spandler et al. 2004). (d–g) Backscattered electron images. (d) Monazite crystal from a migmatite from Sikkim, Himalaya, with two distinct growth zones formed during metamorphism (Rubatto et al. 2013). (e) Allanite grain from an amphibolite facies rock the Central Alps, Switzerland (courtesy of Katherine Boston, ANU). The spectacular zoning corresponds to different allanite compositions. Both the inner core and the outer rim could be dated and constrain different metamorphic stages. (f) Breakdown of allanite to monazite in a metapelite of the Central Alps, Switzerland. The distinct ages of allanite and monazite define a heating rate during collision of 8–15 °C/Ma



Uranium-Lead, Metamorphic Rocks, Fig. 1 (continued) (Janots et al. 2009). (g) Core-rim zoning in a titanite from a calcsilicate of the ultrahigh-pressure unit of Dora Maira, Western Alps, Italy. The core and rims formed at different pressure (HP and LP: high and low pressure), and their age defines a fast exhumation rate of 3.4 cm/year (Rubatto and Hermann 2001). Circles indicate the location of ion microprobe U–Pb analyses

techniques are carried out with scanning electron microscopes; they cause little or no damage to the sample and are relatively fast to acquire.

Materials

Minerals used for U–Pb dating in metamorphic rocks are numerous and include zircon (ZrSiO_4), monazite $[(\text{La}, \text{Ce}, \text{Nd}, \text{Th})\text{PO}_4]$, allanite $[(\text{Ca}, \text{REE}, \text{Th})_2(\text{Fe}^{2+}, \text{Al})_3\text{Si}_3\text{O}_{12}(\text{OH})]$, titanite (CaTiSiO_5), rutile (TiO_2), and, less commonly, baddeleyite (ZrO_2).

Zircon and monazite are the most commonly dated U–Th minerals and offer specific advantages when dating metamorphism. Because the diffusion of Pb is particularly slow in these two minerals, they preserve their U–Pb formation age even if heated to high metamorphic temperatures (800–900 °C) or if the host rock is chemically altered. This allows zones in inherited zircons that have overgrowths formed during metamorphism to be separated from ones that grow during metamorphism. Additionally, both minerals commonly develop multiple growth zones that may preserve a record of more than one metamorphic stage (Fig. 1). Metamorphic zircons can form in a variety of conditions virtually covering all metamorphic grades, but are most common at high pressure (Rubatto and Hermann 2007) and/or high temperatures, particularly in the presence of melt (Rubatto et al. 2001). Dating of metamorphic zircon has shed light on the age of metamorphism from the earliest records of plate tectonic (Friend and Nutman 2005) to the youngest exhumed eclogites (Baldwin et al. 2004). Unlike other U–Th minerals, zircon commonly preserves a record of the pre-metamorphic history, be it magmatic or sedimentary. Metamorphic growth zones can be distinguished on the basis of their zoning and composition. Zoning is most commonly weak and/or not polygonal. A low Th/U content is typical of most metamorphic zircon because of coexisting phases like monazite or allanite sequester Th. The trace element composition of metamorphic zircon can also be diagnostic (see below and Hoskin and Schaltegger 2003). Another quality of metamorphic zircon is its physical robustness and capacity to act as a container of mineral inclusions (Fig. 1a). A challenging aspect of dating metamorphic zircon is that it may contain lower amount of U and Th than magmatic zircon and thus have weak radiogenic signal. This results in a high percentage of initial Pb and large analytical errors. Therefore, U–Pb analyses of metamorphic zircon are commonly plotted in uncorrected “Tera-Wasserburg” diagrams, where the age is determined by the free regression of multiple data points (Fig. 2a).

Monazite is particularly appealing to date metamorphism because it has similar qualities to zircon, but is more reactive to metamorphism (Rubatto et al. 2001). It readily forms in metapelites (fine-grained metamorphosed sediments) and some metagranitoids (metamorphosed igneous aluminosilicate-rich rocks) from diagenesis to granulite facies and can preserve multiple growth zones of different age (Fig. 1d). It contains significant amounts of U and Th and both systems can be used for age determination.

Allanite is common in Ca-rich metamorphic rocks. Like monazite, it can preserve multiple metamorphic growth zones (Fig. 1e). Monazite and allanite both contain significant amounts of light rare earth elements and thus commonly show mutual replacement textures (Janots et al. 2008) that are valuable for age interpretation (Fig. 1f). Unlike most other U–Th minerals, allanite

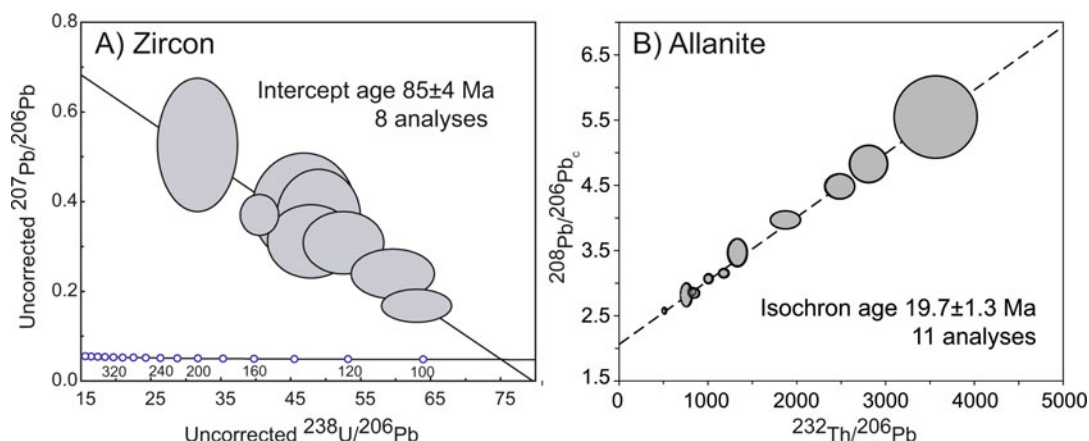


Fig. 2 (a) Tera-Wasserburg diagram of ion microprobe (SHRIMP) analyses of very low U (1–6 ppm) zircon from an eclogite. The proportion of initial Pb in the analyses is between 15 % and 60 %. The date is given by the lower intercept of the regression line with the reverse Concordia curve. (b) Th–Pb isochron for LA-ICPMS analyses of metamorphic allanite. The isochron gives an accurate age despite the uncertainty on the composition of the initial Pb (Gregory et al. 2012). Pb_c denoted the non-radiogenic Pb component. Data are plotted with two sigma errors and average ages are given at 95 % confidence level

incorporates a significant amount of Pb during growth, particularly in sub-solidus metamorphic rocks (Gregory et al. 2012). This initial Pb can severely hamper the precision of U–Pb dating and requires a particular analytical treatment, such as independent measurement of initial Pb or Th–Pb isochrons (Fig. 2b). Because allanite contains more Th than U, the Th–Pb system is generally less contaminated by initial Pb and thus most reliable for age determination.

Rutile is an appealing mineral to date metamorphism because it mainly forms in metamorphic environments, most commonly in high pressure and temperature rocks, and it can be used as a thermometer (Zack et al. 2004). However, this oxide does not necessarily contain enough uranium – and no Th – and thus its radiogenic signal may be too weak to be measured accurately. The concentration of U in rutile is particularly low in mafic rocks (i.e., eclogites), whereas rutile in metasediments and granitoids can be richer in U, especially if metamorphosed at high temperature (Vry and Baker 2006; Kooijman et al. 2010; Ewing et al. 2013). Because rutile does not seem to preserve metamorphic growth stages, it is suitable for bulk dating by isotope dilution thermal ionization mass spectrometer (TIMS) that can achieve better precision. The diffusion of Pb in rutile and thus the potential to reset the radiogenic signal is relatively fast compared to the other U–Th-bearing minerals (Cherniak 2000; Kooijman et al. 2010). This makes rutile most suitable to date metamorphic stages below ~ 600 °C.

Titanite is a common U-bearing mineral in metamorphic rocks of variable composition. Its role as geochronometer is limited by low U and thus radiogenic Pb contents and high proportion of initial Pb (Romer 2001). As for rutile, titanite in mafic rocks is particularly difficult to date, and best results have been obtained for titanite in metasediments (Kohn and Corrie 2011), including metacarbonates (Rubatto and Hermann 2001).

Baddeleyite forms in silica-undersaturated rocks, i.e., mafic and ultramafic rocks free of quartz. It is commonly used to date mafic dikes, but can occasionally form during metamorphism (Rubatto and Scambelluri 2003). It shows internal zoning similar to zircon.

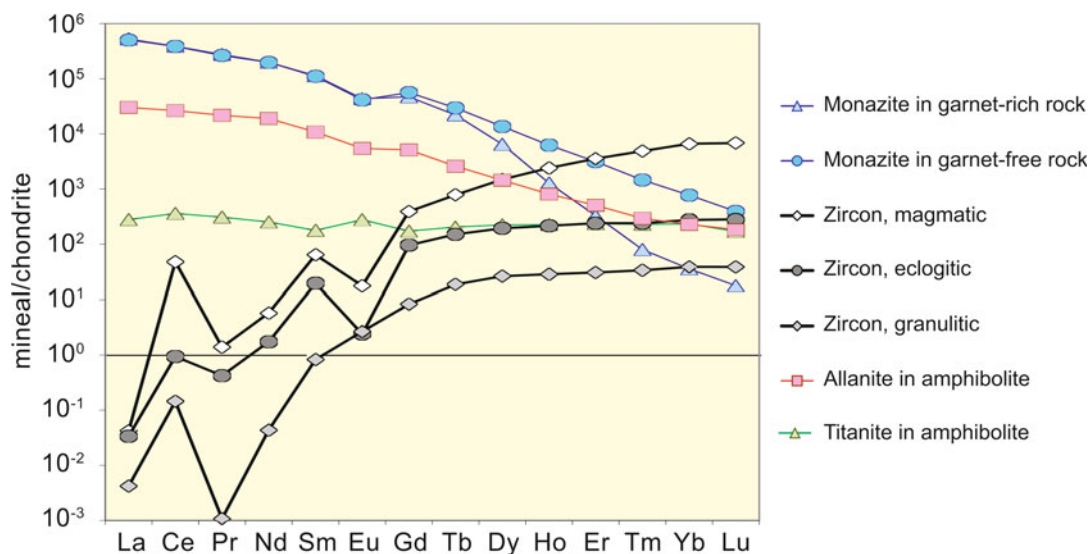


Fig. 3 Rare earth element patterns of U–Pb accessory minerals in different metamorphic assemblages. Patterns are normalized to chondrite values

Dating of Metamorphic Stages

The necessary connection between a measured U–Pb age and the metamorphic stage/reaction that such an age constrains can be achieved via different methods. Inclusions of metamorphic minerals in dated mineral zones can be a direct indication of when the dated mineral formed. For example, inclusion of high-pressure minerals, such as diamond (Fig. 1a) or coesite, in zircon indicates that the zircon formed above a certain pressure. Together with inclusion relationships, other textural relationships with main rock-forming minerals can be useful to determine at which metamorphic stage a U–Th mineral crystallized. However, because accessory minerals are often small in size and can be inherited to the metamorphic mineral assemblage, such relationships are not always straightforward.

Occasionally, the formation of U–Th minerals during metamorphism can be traced back to a specific reaction. Examples are formation of micro-zircons during garnet breakdown (Degeling et al. 2001), the reaction between allanite and monazite that involves other minerals (Fig. 1f) (Janots et al. 2008), and the rutile-titanite transformation. These are rare cases and most commonly U–Th minerals form by recrystallization or dissolution-precipitation of preexisting crystals.

Accessory mineral thermometry is another direct way to establish the temperature at which a dated mineral zoned formed. The Ti-in-zircon (Watson et al. 2006) and the Zr-in-rutile thermometers (Zack et al. 2004) are both based on the trace element composition (Ti and Zr respectively) of two minerals that can be dated by U–Pb. Because the diffusion of Zr and Ti is slow, these thermometers are robust up to extreme metamorphic temperatures. In metapelites containing monazite, xenotime (YPO₄), and garnet, the content of Y- and heavy-REE in monazite depends on temperature and can be used as a thermometer (Heinrich et al. 1997; Pyle et al. 2001).

The partitioning of trace elements between U–Th minerals and major rock-forming minerals can be used to link ages to specific assemblages. Most of the U–Th minerals are rich in trace elements, particularly yttrium and rare earth elements (REE, Fig. 3). Their Y-REE composition depends on the composition of the rock and the abundance of other coexisting minerals that contain significant amounts of such elements, including garnet for Y- and heavy-REE and feldspar for europium and strontium. For this reason, variation in trace element contents and specific REE patterns are typical

of certain assemblages (Fig. 3). Zircon that forms at high pressure develops a REE signature particularly low in heavy-REE and with no Eu anomaly (Rubatto 2002). Zircon in granulites is relatively depleted in heavy-REE and has a strong negative Eu anomaly due to coexistence with abundant garnet and feldspars. Similarly monazite that has grown in a garnet-rich assemblage will have a particularly strong depletion in heavy-REE. High-pressure monazite, that has grown in a feldspar-free assemblage, is also rich in Sr (Finger and Krenn 2007). This approach is particularly powerful if variations in trace element composition are seen in distinct growth zone of the same crystal (Hermann and Rubatto 2003; Xia et al. 2009; Rubatto et al. 2013).

Conclusions and Future Prospectives

Our ability to date U–Th minerals in metamorphic rocks is currently limited by the capacity to sample small growth zones and measure their age with high precision. In the future, further developments of micro-sampling using microbeam techniques, as well as increased analytical sensitivity and precision for very small sample volumes and low radiogenic samples, will greatly benefit U–Pb dating of metamorphism.

The interpretation of ages in terms of rock evolution (pressure, temperature, fluids, and deformation) is the other limiting factor. The discovery of new geothermometers and geobarometers based on U–Th minerals would make a significant difference in our capacity to constrain the time of metamorphic stages. Similarly, advances in the understanding of the petrological behavior of such minerals and improvements in the thermodynamic modeling of their P–T stability would greatly assist age interpretation.

Cross-References

- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Secondary Ion mass spectrometer \(SIMS\)](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Uranium-Lead, Chemical Isochron U-Pb Method \(CHIME\)](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)
- ▶ [Uranium-Lead, Igneous Rocks](#)
- ▶ [Uranium-Lead, Zircon](#)

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Amino Acid Racemization, Marine Sediments

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Definition

Amino acid racemization. The phenomenon of conversion of “left-handed” (L or “levo”) amino acids to their “right-handed” (D or “dextro”) form. In most living systems, 100 % of the amino acids are of the L form, and the conversion results in an equal mixture of D and L when the racemization reaction is complete.

Marine Sediment. Material that accumulates in the marine environment. This article focuses on material collected in cores from deep-sea settings.

Among the wide range of applications of amino acid geochronology, this technique is especially well suited for dating deep-sea sediments using foraminifera. Foraminifera inhabit most of the World Ocean and they contain relatively high concentrations of amino acids that are well retained by their carbonate test. The stable thermal environment of deep-sea sites minimizes the often-complicating effect of variable temperature on the long-term rate of racemization. Some of the earliest research on amino acid geochronology took advantage of the long-term stability of deep-sea settings to investigate the diagenesis of amino acids over geologic time, including the rate of racemization in foraminifera (Wehmiller and Hare 1971; Bada and Schroeder 1972; King and Hare 1972; Kvenvolden et al. 1973; Schroeder and Bada 1977; Bada et al. 1978; Bada and Man 1980; King 1980; Belknap and Doyle 1986; Stathopulos et al. 1987; Robbins and Brew 1990). The extent of amino acid racemization in fossil foraminifera has also been used to estimate the ages of Quaternary marine sediment (Müller 1984; Macko and Aksu 1986; Sejrup and Hughen 1992; Knudsen and Sejrup 1993; Murray-Wallace and Belperio 1994; Harada et al. 1996), and in a few cases, to reconstruct paleotemperature histories (Bada and Man 1980; Lehman et al. 1988; Johnson et al. 1990).

Two general approaches can be used to convert the extent of amino acid racemization to a numeric time scale: In the first approach, the effects of time and temperature on the extent of racemization are determined in modern shells subjected to high-temperature laboratory experiments (e.g., Kaufman 2006). This relation, together with a model of racemization kinetics, is used to calculate the age of a sample if its temperature history is known. Because accelerating the rate of racemization under high temperature may not precisely mimic the net effect of long-term diagenetic processes, most attempts to quantify the temperature sensitivity of long-term racemization extend their analyses to ambient temperatures and geologic environments by including analyses of Holocene samples whose ages are known from radiocarbon dating, and whose temperature history can be reasonably inferred from instrumental measurements. A more secure approach that does not require assumptions about temperature history is to calibrate the rate of racemization by analyzing securely dated samples of a particular taxon from a region where temperature histories are uniform (Sejrup et al. 1984; Harada and Handa 1995; Hearty et al. 2004; Kaufman et al. 2008, 2013). The calibrated reaction rate is then used to date samples of the same taxon of unknown age from the same environment where temperature histories are similar.

Figure 1 shows the extent of aspartic acid racemization (Asp D/L) in independently dated, mono-specific foraminifera samples from the Pacific, Atlantic, and Arctic oceans (Kaufman et al. 2013). These data

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provide the basis for developing a calibrated age equation to apply to undated samples (the second approach described above). Figure 1 also shows the modeled rate of racemization based on laboratory-heated and radiocarbon-dated foraminifera for three temperatures (Kaufman 2006). The ages of samples can be determined by analyzing their D/L values and assuming a reasonable temperature history (the first approach).

Most studies of amino acid geochronology based on foraminifera have used gas chromatography or ion-exchange HPLC to separate the D- and L-amino acids, both of which require hundreds of foraminifera tests for a single analysis (several milligrams of fossils). Consequently, these studies relied on samples of mixed foraminiferal taxa. Sample size requirements using HPLC reverse-phase chromatography (RPC) are at least two orders of magnitude lower (Kaufman and Manley 1998), allowing analysis of fewer, and even single specimens in the case of a taxon with a large test (Hearty et al. 2004). Subdividing a sample into small subsamples, each analyzed individually, can improve the accuracy of the results because collections of microfossils commonly include a few individuals whose D/L values fall outside the mean of the others. These outliers might result from post-depositional reworking, post-collection contamination, or an aberrant diagenetic pathway. Regardless of the cause, by routinely analyzing multiple subsamples per level (10 or more), these aberrant results can be identified objectively and excluded from the data set. The resulting mean D/L values are more accurate than those based on just a few subsamples.

The rate of racemization differs among foraminifera taxa. An early investigation of mono-specific samples (King and Neville 1977) showed that the extent of racemization (epimerization of isoleucine) in different taxa from the same level within a sediment core could differ by as much as a factor of 4 between species. More recent analyses based on the same approach and augmented by laboratory heating experiments do not show a difference of this magnitude among mono-specific samples, either as fossils or as laboratory-heated specimens (Kaufman et al. 2013). Differences in racemization rates might be

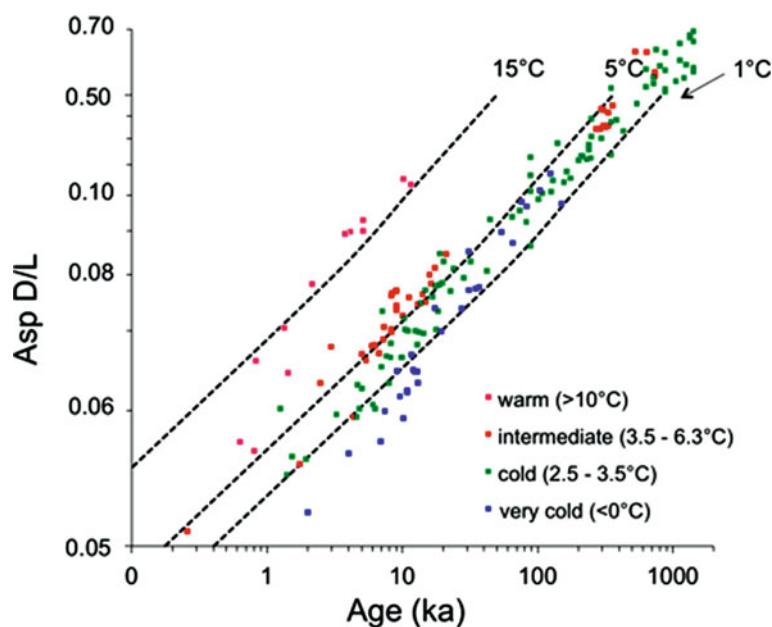


Fig. 1 Extent of racemization (D/L) for aspartic acid (*Asp*) in independently dated samples of all 179 mono-specific foraminifera samples from deep-sea cores in the Pacific, Atlantic, and Arctic oceans extending back to 1.5 Ma (Kaufman et al. 2013). Colors indicate the current site temperature grouped into four categories. In addition, the modeled rate of racemization based on laboratory-heated and radiocarbon-dated *P. obliquiloculata* for three temperatures is shown for comparison (dashed lines; Kaufman 2006). Data are plotted on logarithmic scales to improve data presentation

attributed to the effect of contamination of the type described by Stathoplos and Hare (1993) and Sejrup and Haugen (1992) and that can be recognized by the relatively high serine content (Kaufman et al. 2013).

Previous studies recognized the potential of exogenous amino acids to contaminate foraminifera and to skew the results (Stathoplos and Hare 1993; Sejrup and Huguen 1992). Many studies have investigated the procedures for pretreating samples to isolate the most reliably indigenous amino acid fraction (e.g., Penkman et al. 2008), and for applying data-screening criteria to identify and exclude outliers based on statistical tests of internal consistency among multiple amino acids (e.g., Kosnik and Kaufman 2008). In addition, the concentration of serine, a liable amino acid that is present in only low concentrations in fossils, has been used widely as an indicator of contamination by young amino acids (e.g., Kaufman et al. 2013).

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Hydrocarbons/Rhenium–Osmium (Re–Os): Organic-Rich Sedimentary Rocks

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Definition

Utilization of the rhenium–osmium (Re–Os) radioisotope geochronometer to (1) determine the depositional age of organic-rich rocks (ORR), (2) establish the Os isotope ($^{187}\text{Os}/^{188}\text{Os}$) composition of sedimentary successions, and (3) date the timing of hydrocarbon (oil) generation related to thermal maturation of an organic-rich sedimentary rock.

Introduction

The first application of the Re–Os isotope geochronometer to ORR demonstrated that the Re–Os data, although imprecise, could yield the depositional age of sedimentary successions (Ravizza and Turekian 1989), a remarkable outcome given the analytical challenges and data uncertainties at the time. Today, utilizing new analytical and mass spectrometry techniques (see below) and the most accurate ^{187}Re decay constant ($1.666 \times 10^{-11} \text{ year}^{-1}$; Smoliar et al. 1996) has permitted the determination of precise (in some cases $\leq 1\%$ uncertainty) depositional ages for ORR that possess $\geq 0.5 \text{ wt\%}$ total organic carbon (TOC) (e.g., Cohen et al. 1999; Georgiev et al. 2011; Kendall et al. 2009a; Selby and Creaser 2005a; Xu et al. 2009; Cumming et al. 2012). These studies have provided the foundation to apply the Re–Os organic-rich sedimentary rock geochronometer to yield ages throughout geological time for stratigraphic boundary intervals and major Earth events (e.g., rise of oxygen, Proterozoic glaciations etc.; Selby and Creaser 2005a; Selby 2007; Anbar et al. 2007; Xu et al. 2009; Rooney et al. 2011; Yang et al. 2009).

Rhenium–osmium geochronology of ORR utilizes the isochron method, which yields the initial Os isotope composition ($^{187}\text{Os}/^{188}\text{Os}$) for the sampled unit, taken to represent the $^{187}\text{Os}/^{188}\text{Os}$ composition of the water column at the time of deposition (Ravizza and Turekian 1989; Cohen et al. 1999; Peucker-Ehrenbrink and Ravizza 2000, 2012).

In addition to ORR, hydrocarbon products of such matured rocks, for example, crude oil and bitumen, have been shown to also be enriched in both Re and Os at the ppb and ppt level, respectively (Barre et al. 1995; Woodland et al. 2001; Selby and Creaser 2005b; Selby et al. 2007; Finlay et al. 2011). The hydrocarbon Re–Os isotope data from several petroleum systems has shown that Re–Os systematics of hydrocarbons can provide the timing of petroleum generation from an oil source rock (Selby et al. 2005; Selby and Creaser 2005b; Finlay et al. 2011), with the initial $^{187}\text{Os}/^{188}\text{Os}$ value derived from Re–Os hydrocarbon data interpreted to reflect the $^{187}\text{Os}/^{188}\text{Os}$ inherited from the source rock at the time of petroleum expulsion (Selby and Creaser 2005b; Rooney et al. 2012).

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Methodology: Analytical Protocol and Sampling

Since the pioneering application of the Re–Os chronometer to dating of ORS (Ravizza and Turkeian 1989), significant analytical advancements in digestion methods, chemical purification, and mass spectrometry have permitted the determination of precise Re–Os data. Current methods employ analysis of an aliquot of ground organic-rich rock digested in either inverse aqua regia (3:6 ml mix of concentrated HCl:HNO₃) or 8 ml of 4 N H₂SO₄ with 0.25 g/g CrO₃ along with a known amount of isotope tracer solution (¹⁸⁵Re + ¹⁹⁰Os) in a Carius tube at 220°C for 48 h (Cohen et al. 1999; Selby and Creaser 2003). The use of the Cr^{VI}–H₂SO₄ digestion method has been shown to limit the release of detrital Re and Os from organic-rich rock matrices and as a result reduce the scatter about the line of an isochron (Selby and Creaser 2003; Kendall et al. 2004). The inverse aqua regia medium is used for the digestion of hydrocarbons, such as asphaltene and bitumen. Osmium from the acidic solution is typically isolated and purified by solvent extraction (CCl₄ or CHCl₃) and microdistillation (Cohen et al. 1999; Selby and Creaser 2003; Selby et al. 2007). The Os extracted acidic solution is then used to isolate and purify the Re fraction of the sample. This is achieved by solvent extraction methods and anion chromatography (Selby and Creaser 2003; Chen et al. 2010). The isotope compositions of the purified Re and Os fractions are commonly determined by negative thermal ionization mass spectrometry (Creaser et al. 2002 and references therein).

Re–Os organic-rich rock geochronology requires samples that have not been significantly affected by postdepositional processes such as weathering (Peucker-Ehrenbrink and Hannigan 2000), metamorphism (above greenschist grade; Kendall et al. 2004), and hydrothermal fluid flow (Kendall et al. 2009b; Rooney et al. 2011), in order to minimize any postdepositional mobilization of Re and Os (Kendall et al. 2009a). The application of the isochron method for geochronology requires two principal criteria: (1) the sample set possesses the same or near-identical initial ¹⁸⁷Os/¹⁸⁸Os, but has varied parent/daughter ratios (¹⁸⁷Re/¹⁸⁸Os), and (2) the isotope systematics is not disturbed. At this time, there is no proxy to determine if a section will have both homogeneous initial ¹⁸⁷Os/¹⁸⁸Os and variable ¹⁸⁷Re/¹⁸⁸Os (cf. Turgeon et al. 2007; Cumming et al. 2012). A review of sampling protocols employed in various studies suggests intervals ranging from a few centimeters to several meters can be used to produce precise ages, with at least 20 g of powdered sample required to achieve sample Re–Os homogeneity (cf. Creaser et al. 2002; Kendall et al. 2009a).

Hydrocarbon Re–Os geochronology analysis utilizes either the asphaltene isolated from crude oil or bitumen (Selby et al. 2007). To date, sampling from wells across an oil field has provided Re–Os data sets that have given valuable age information to determine the timing of hydrocarbon generation (Selby et al. 2005; Selby and Creaser 2005b; Finlay et al. 2011; Lillis and Selby 2013).

Organic-Rich Rocks: Rhenium–Osmium Geochronology and Systematics

Rhenium and Os are organophilic, enabling the uptake of hydrogenous Re and Os into organic matter during deposition of ORS (Ravizza and Turekian 1989; Cohen et al. 1999; Selby and Creaser 2003). The Re and Os concentrations in marine and lacustrine ORS range from average upper-crustal abundances (0.2–1 ppb Re and 30–50 ppt Os; e.g., Peucker-Ehrenbrink and Jahn 2001) to several hundred ppb/ppt of Re and Os, respectively (e.g., Baioumy et al. 2011; Cohen et al. 1999; Creaser et al. 2008; Georgiev et al. 2011; Rooney et al. 2010; 2011; Poirier and Hillaire-Marcel 2011; Cumming et al. 2012). Although organophilic, Re and Os abundances do not always

correlate to TOC despite the majority of these metals being held within the kerogen (Rooney et al. 2010, 2012; Cumming et al. 2012).

From the first Re–Os ORR study (Ravizza and Turekian 1989), numerous studies have reported accurate and precise Re–Os depositional ages of organic-rich marine and lacustrine sedimentary units (e.g., Cohen et al. 1999; Creaser et al. 2002; Cumming et al. 2012; Turgeon et al. 2007; Rooney et al. 2011; Xu et al. 2009). Studies also indicate that hydrocarbon maturation and/or low-grade metamorphism does not appreciably disturb the Re–Os systematics (Kendall et al. 2004; Rooney et al. 2010, 2011, 2012; Yang et al. 2009). In contrast to studies yielding highly precise Re–Os ages, the Re–Os data for the Aptian/Albian, Cenomanian/Turonian, and Frasnian–Famennian stage boundaries give accurate, but imprecise ages (Turgeon et al. 2007; Selby et al. 2009). This imprecision is attributed to the limited spread in $^{187}\text{Re}/^{188}\text{Os}$ ratios, highlighting the need for variation in $^{187}\text{Re}/^{188}\text{Os}$ ratios but no variation in initial $^{187}\text{Os}/^{188}\text{Os}$ to produce precise Re–Os dates. The lack of spread is considered to be due to exhaustion of the Re reservoir due to increasing anoxia leading up to the Frasnian–Famennian boundary (Turgeon et al. 2007). However, no correlation is evident between redox conditions and $^{187}\text{Re}/^{188}\text{Os}$ values of ORS (Selby et al. 2009). Alternatively, organic matter type may control Re–Os fractionation in ORS (Cumming et al. 2012; Harris 2012).

Rhenium–Osmium Hydrocarbon Geochronology and Systematics

Petroleum exploration is often hampered by the lack of spatial and temporal controls on hydrocarbon formation. Traditionally, dating the timing of hydrocarbon generation involves basin modeling using estimated parameters (e.g., Ruble et al. 2001). Therefore, knowing the absolute age of petroleum generation provides vital constraints for elucidating petroleum maturation and migration. A pioneering study (Selby et al. 2005) provided evidence of the ability of the Re–Os hydrocarbon geochronometer by yielding an accurate age for bitumen (374.9 ± 9 Ma) from the Polaris Mississippi-Valley-type deposit, Canada, that was in agreement with paleomagnetic and Rb–Sr sphalerite age constraints for mineralization. Further to this, the Re–Os geochronometer has also been applied to the tar sands of the Western Canadian Sedimentary Basin and provided an accurate age (112 ± 5.3 Ma) for the timing of hydrocarbon generation, suggesting that Re–Os hydrocarbon geochronology records the age of oil generation (Selby and Creaser 2005b). A subsequent Re–Os study of oils from the UK Atlantic margin oil fields provided a Re–Os generation age of 68 ± 13 Ma that agrees with basin models and Ar–Ar ages for K-feldspars bearing oil-rich fluid inclusions and demonstrated that the Re–Os hydrocarbon systematics is unaffected by biodegradation (Finlay et al. 2011).

Both Re and Os in hydrocarbons have been shown to be held in the heavy molecular fraction of oil (asphaltene) and suggested to reside within metalloporphyrins similar to Ni and V or heteroatomic ligands due to their abundance in asphaltene. The asphaltene fraction is shown to possess the same isotopic compositions to that of the whole oil. This study advanced the analytical application of this tool as the separation of asphaltene for Re–Os analysis allows much higher abundances to be analyzed, yielding more precise Re–Os data (Selby et al. 2007).

Oil-to-source correlation is most commonly carried out by using carbon isotopes and/or biomarkers, but these methods can be hampered by biodegradation as they rely on the light fractions of oil that are removed by biodegradation (Peters et al. 2005). The initial $^{187}\text{Os}/^{188}\text{Os}$ value derived from the Re–Os hydrocarbon data is interpreted to reflect the $^{187}\text{Os}/^{188}\text{Os}$ inherited from the source rock at the time of petroleum expulsion (Selby and Creaser 2005b; Selby et al. 2005, 2007; Finlay

et al. 2011, 2012). The reliability of Os as an oil-to-source fingerprinting tool was further corroborated experimentally (Rooney et al. 2012). This involved artificial maturation of the source rocks coupled with Re–Os analysis of the original rocks and the products derived from the hydrous pyrolysis experiments in order to assess transfer of Re and Os from source to oil. The $^{187}\text{Os}/^{188}\text{Os}$ compositions in bitumens were found to be the same as their source rock in both units studied, providing strong evidence that Os isotopes can be used as powerful oil-source correlation tools.

Although the petroleum Re–Os systematics is not appreciably disturbed, biodegradation studies have indicated that the systematics can be affected by the interaction of mantle fluids (Finlay et al. 2011) and TSR (Lillis and Selby 2013). These studies demonstrated the importance of Os in understanding crustal-scale fluid dynamics, oil migration pathways, and Re–Os hydrocarbon systematics.

Summary

Rhenium–osmium analysis of marine and/or lacustrine ORR permits the age of deposition of the sediment to be established. This method also yields the osmium isotope composition of the water column associated with the deposition of the sediment. The Re–Os systematics of ORR is not disturbed by processes associated with oil generation and/or low-grade metamorphism. Rhenium–osmium analysis of oil generated and migrated from ORR has been shown to yield the timing of hydrocarbon maturation. Further the petroleum Os isotope data have been shown to be a potentially powerful tool to aid in fingerprinting an oil-to-source ORR.

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Molecular Dating of Evolutionary Events

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Definition

Inference of the age of evolutionary events using statistical analysis of rates of change of DNA or amino acid sequences.

Introduction

Molecular dating is used in the biological sciences to estimate the age of evolutionary events. Changes to DNA and amino acid sequences accumulate continuously in the genome over time, so comparing DNA sequences between lineages allows us to estimate the time since they last shared a common ancestor. However, the rate of change varies across the genome and among species. So in order to use molecular data to date evolutionary events, we need a way of estimating the rate of change in genetic sequences over time for any given dataset. Molecular dating requires a set of homologous genetic sequences (all related by descent from a single ancestral sequence), a method for inferring the number of changes that have occurred during the evolution of these sequences, and calibrating information to estimate their rate of change.

An increasing variety of analytical tools are available for molecular dating of evolutionary events. All assume that the rate of genetic sequence evolution has some degree of predictability, so that the age of lineage divergence can be estimated from molecular data using a model of evolutionary change and some information about timing of evolutionary events (typically derived from fossils, biogeography, pedigree, or ancestral genetic sequences).

Methods for Dating Evolutionary Events

Molecular dating methods begin by estimating the amount of genetic difference that has occurred between sequences. Then, assumptions about the rate of change are used to infer the amount of time needed to explain that amount of genetic difference. The difference between genetic sequences is estimated using a model of the frequency of each type of substitution. Models of molecular evolution form the basis of methods to estimate the relatedness of multiple sequences and the timing since their evolutionary divergence (for more detail on the models, see Yang 2006). These models can be simple and give an equal probability to every type of substitution (Jukes and Cantor 1969), or be complex and account for the attributes of specific genetic datasets (e.g., Yang 1994). For instance, the mitochondrial ND6 genetic region in marine mammals has virtually no transversions (changes from the purines, A and G, to pyrimidines, C and T, or vice versa), so it

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is appropriate to use parameter settings that model a large number of transitions (changes from purine to another purine, or pyrimidine to pyrimidine) (Duchêne et al. 2011).

The simplest way to use genetic difference estimates to infer the timing of evolutionary divergences is to select “clocklike” data, where the amount of genetic difference accumulates at the same rate in all lineages. There are methods to detect significant variation in rates (Langley and Fitch 1973; Takezaki et al. 1995). For example, Likelihood Ratio Test can be used to ask whether data can be best described by a single uniform rate, or a multiple rate model (Brown and Yang 2011). Importantly, while some datasets may approximate uniform rates, clocklike behavior cannot be generalized to a particular gene, lineage, or taxonomic level.

Another way to account for rate variation is to have multiple rate categories in the same analysis. For example, sections of the dataset may have their own “local clock” (Drummond and Suchard 2010; Rambaut and Bromham 1998; Yoder and Yang 2000). Other methods account for rate variation by “relaxing” the molecular clock constraint on all branches, so every branch in a phylogeny has a different rate (e.g., Drummond et al. 2006; Yang 2007); for more on this topic, see Springer Reference article Relaxed Molecular Clocks; for reviews on dating methods, (see Magallón 2004; Rutschmann 2006; Welch and Bromham 2005).

Calibrating the Rate of Substitutions

Some molecular dating analyses use an assumed rate of substitutions to estimate dates. However, given that rates of molecular evolution vary across the genome and between lineages, it is preferable to use independent information to calibrate rates of molecular evolution for each dataset analyzed. The most common way of calibrating rates is to use a known date of one or more divergence events in the phylogeny.

The calibration must correspond to the earliest possible age of a node in the phylogeny. The dates of divergence events are rarely known with certainty, and the confidence limits on calibrations can be very large. In the case of fossil evidence, part of the uncertainty comes from the determination of the age of the fossil itself, drawn from stratigraphy and isotopic composition of the fossil (Benton and Donoghue 2007). However, the exact relationship between the fossil taxon and the divergence in the phylogeny is also typically unknown (Sauquet et al. 2012). A fossil taxon is unlikely to be identifiable as a member of a particular lineage until some time after the origin of the lineage, when key diagnostic characters have had time to evolve. So fossil dates typically represent minimum ages of lineages: they provide evidence that a lineage must have originated some time before that date (Bromham et al. 1999).

One way to account for calibration uncertainty is to have a probability distribution of node ages. A hard-bound can define the latest or the earliest point where a divergence may have occurred (also called the minimum age and the maximum age, respectively). While a minimum age can be defined by the age of a fossil known to occur on the lineage in question, because the lineages must have originated before the occurrence of the first fossil, special caution is required when placing a maximum constraint because it assumes with total confidence that a lineage was absent before a given time (Benton and Donoghue 2007; Ho and Phillips 2009; Hug and Roger 2007).

To overcome the strict assumptions of hard-bounded calibrations, an alternative is to use soft-bounded calibrations, so a nonzero probability can be assigned to all ages (Yang and Rannala 2006). To define a soft-bounded calibration, the user must specify a probability distribution for the date of the calibrating divergence. Given that the confidence in particular date estimates is specific to current knowledge, expert advice is often required to define these calibrations. Broadly,

a normally distributed calibration is conservative for fossil data that is imprecise or equivocal. A normally distributed calibration can also be used for biogeographic data that provides reasonable evidence for causing a divergence event, or for calibrations based on previous date estimation analyses (also called secondary calibrations, Ho and Phillips 2009). Lognormal distributions are often appropriate for fossil data as they provide a hard minimum bound, which is the age of the fossil. They also allow a higher probability for the divergence of a node at a point slightly older than the age of the fossil. These distributions are also applied when using previous date estimates from Bayesian analyses that produced lognormal distributions.

Exponentially distributed calibrations can be used if there is little evidence that an event occurred at any point before the fossil, or if the fossil is likely to be very close to the divergence event (Ho and Phillips 2009). To choose the values of the parameters of these distributions, the user must be well informed about the sources of error in the calibration. Poor calibrations may be useful if their uncertainty can be quantified, but if only poor calibrations are used, then the uncertainty in date estimates will be significant.

Summary and Conclusions

The field of molecular dating of evolutionary events can be divided by the methods to deal with variation in the rate of molecular substitutions. To date evolutionary events using molecular data, it is necessary to evaluate and choose a method to model molecular evolution. It is also necessary to find information to calibrate rates of substitutions, and all analyses must account for calibration uncertainty. Although modern software for this purpose can be deceptively simple, there is a plethora of considerations required before performing molecular dating analyses. In particular, Bayesian methods for molecular dating can involve complex assumptions about the model of molecular evolution and arguably are not entirely understood. Methods in place to compare and choose the most appropriate dating schemes are computationally demanding and may be severely biased (Baele et al. 2012; Lartillot and Philippe 2006; Xie et al. 2011). However, with appropriate information and a clear understanding of the uncertainty inherent in molecular date estimates, molecular dating is a powerful tool that can be extended to study the realms of evolution, ecology, biogeography, and past population processes.

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Tephrochronology

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Synonyms

[Chronostratigraphy](#); [Stratigraphic correlation using tephra](#); [Tephrostratigraphy](#)

Definitions

Tephra. All the explosively erupted, unconsolidated pyroclastic products of a volcanic eruption.

Cryptotephra. Tephra-derived glass-shard and/or crystal concentration preserved in sediments or soils/paleosols but not visible as a layer to the naked eye.

Tephrostratigraphy. Study of sequences of tephra layers or cryptotephra (and associated deposits) and their lithologies, spatial distribution, stratigraphic relationships, and relative and numerical ages. Involves defining, describing, characterizing, and dating tephra layers or cryptotephra deposits in the field and laboratory as a basis for their correlation.

Tephrochronometry. Obtaining a numerical age or calendrical date for a tephra or cryptotephra deposit.

Tephrochronology sensu stricto. The use of primary tephra layers or cryptotephra as isochrons to connect and synchronize depositional sequences, or soils, and to transfer relative or numerical ages to the sequences using lithostratigraphic, compositional, and other data pertaining to the tephras/cryptotephra.

Tephrochronology sensu lato. All aspects of tephra/cryptotephra studies and their application.

Introduction and Definitions

Tephras are the explosively erupted, unconsolidated pyroclastic (fragmental) products of a volcanic eruption (Greek *tephra*, “ashes”) (Lowe 2011). Typically they comprise volcanic glass (including shards, pumice, and scoriae or cinders), rock (lithic) fragments, and crystals (mineral grains), which are erupted through the atmosphere and deposited on the land, the seafloor, or ice caps relatively quickly – usually in a matter of hours or days according to eruption duration (Lowe 2011; Stevenson et al. 2012). A tephra layer deposited from a powerful eruption, and not reworked, consequently forms a widespread, thin blanket on the surface of the Earth that has effectively the same age – an isochron – wherever it occurs. The term “tephra” encompasses all grain sizes: ash (grains <2 mm in diameter), lapilli (64–2 mm), or blocks (angular) or bombs (rounded) (>64 mm) (White and Houghton 2006). Diminutive, distal tephras that are not visible as layers in the field are called cryptotephra (Greek *kryptein*, “to hide”). Cryptotephra comprise concentrations of ash-sized glass

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Fig. 1 Stratigraphic sequence of four Holocene tephra deposits of ash and lapilli grade, and buried soil horizons, near Mt Tarawera, New Zealand. Exposure is ~2 m high. From *top*, Tarawera tephra (mainly Rotomahana Mud member) (erupted 10 June 1886); shower-bedded Kaharoa tephra ($AD\ 1314 \pm 12$), characterized by abundant biotite; Taupo tephra ($AD\ 232 \pm 10$) (note that the *gray* and *dark-brown* soil horizons evident in the upper part of the nonwelded Taupo deposit, Taupo ignimbrite, are the result of podzolization, an acidic soil-leaching process that occurred here prior to the soil's burial by the Kaharoa eruptives); and Whakatane tephra ($5,526 \pm 145$ cal. year BP) (ages from Lowe et al. 2013) (Photo: Megan Balks)

shards or crystals, or both, usually $<150\ \mu\text{m}$ in diameter, preserved in sediments (including ice), in cave deposits, or in soils or paleosols (Lowe 2011; Lane et al. 2014).

Tephrochronology may be defined as the use of primary tephra layers or cryptotephra deposits as isochronous beds to connect and synchronize depositional sequences and to transfer relative or numerical ages (or dates) to such sequences using stratigraphic information together with lithological, compositional, and geochronological data obtained for the tephtras or cryptotephtras. Tephrochronology is thus a method for correlating and dating geological, paleoecological, paleoclimatic, or archaeological sequences or events, or soils, using characterized tephtras or cryptotephtras as chronostratigraphic marker beds (Alloway et al. 2013).

Tephrochronology is undertaken typically in three steps. Firstly, tephra deposits are correlated from place to place in the field using their lithostratigraphic and relative age relationships along with intrinsic physical properties, associations with other deposits, and spatial distribution, i.e., tephrostratigraphy (Fig. 1). Fieldwork is carried out at a range of scales because tephra deposits become thinner, and constituent components become smaller, from proximal to distal locations. A potential complication is tephra remobilization, which is discussed later. Secondly, the components of the deposits are characterized or “fingerprinted” using mineralogical or geochemical analytical methods, often both, in the laboratory to aid their correlation. Such laboratory characterization is essential in cryptotephra studies. Thirdly, when a numerical age or date for a tephra or cryptotephra deposit is obtained, i.e., tephrochronometry, that age or date can be transferred from

one site to the next by comparing the compositional characteristics or “fingerprints” of its components with those of equivalent deposits elsewhere. These three steps – (i) mapping tephra and determining their lithostratigraphic relationships, (ii) characterizing tephra/cryptotephra in the laboratory, and (iii) dating them – enable tephrochronology to function as a unique stratigraphic and geoscientific dating tool and are described below in detail after a subsection on volcanological applications.

Volcanological Applications of Tephrochronology

As well as providing isochrons for geological, archaeological, and paleoenvironmental applications, tephrochronological studies involving mapping, characterization, and dating are critical for developing a comprehensive record of past explosive eruptions and recurrence rates from which time-space relationships of volcanism can be established and volcanic hazards evaluated (e.g., Óladóttir et al. 2008; Kuehn and Negrini 2010). Knowledge of the distribution and thickness relationships of tephra or cryptotephra deposits enables magma volumes to be calculated (Wilson et al. 2009; Ponomareva et al. 2013a). Near to volcanic centers, deposits may include lavas as well as an array of different types of pyroclastic deposits (fall, surge, flow and density current, and explosion breccias; Fig. 2), and detailed studies of their stratigraphic intercalation and physical, mineralogical, and geochemical properties provide insight into volcanic history and petrogenesis (e.g., Ponomareva et al. 2004; Smith et al. 2005; Turner et al. 2011a; Cioni et al. 2014). Information about the release of volatiles into the atmosphere and associated climatic impacts can also be gleaned from studies on tephra (e.g., Zdanowicz et al. 1999; Alloway et al. 2013; Sigl et al. 2013).

Mapping and Correlating Tephra

The most successful approaches in the field include the so-called hand-over-hand method whereby relatively thick sequences of tephra, typically meter to decimeter scale, at proximal or medial locations, are documented and traced from one outcrop or section to the next using distinctive physical properties in combination with their stratigraphic associations (Fig. 3). Physical properties include color, bedding characteristics, or particle-specific features such as pumice/scoria, lithic, and crystal componentry, the presence of accretionary lapilli, or marker mineral grains (crystals) such as biotite identifiable via a hand lens. Distinctive marker beds provide a useful stratigraphic starting point in unraveling the complexities of geological sequences in road cuttings or natural exposures, and detailed lithostratigraphic columns are constructed to provide the basis essential for correlating from one site to the next (Fig. 3). The nature of buried soil horizons, or loess or other deposits associated with tephra layers, including (for example) fossils or other attendant paleoecological information such as pollen assemblages (e.g., Newnham and Lowe 1999; Housley et al. 2013; Westgate et al. 2013a), or archaeological relationships (Feibel 1999; Mullen 2012; Riede and Thastrup 2013), may provide additional contextual information helpful for affecting correlation (Fig. 4). High-resolution tephrostratigraphic records in Iceland were constructed by Streeter and Dugmore (2013) using digital photography to obtain thousands of stratigraphic measurements of multiple tephra layers intercalated with sediments at a resolution of 1 mm.

One potential difficulty in tephrostratigraphy arises where tephra remobilization has occurred or where glass shards or crystals have been disseminated or dispersed in sediments or soils, and hence primary isochron positions are not clear (Alloway et al. 2004a; Pyne-O'Donnell 2011; Housley et al. 2012). Remobilization of tephra resulting from widespread landscape instability in combination with climatic factors (e.g., Manville and Wilson 2004) can remobilize large volumes of tephra

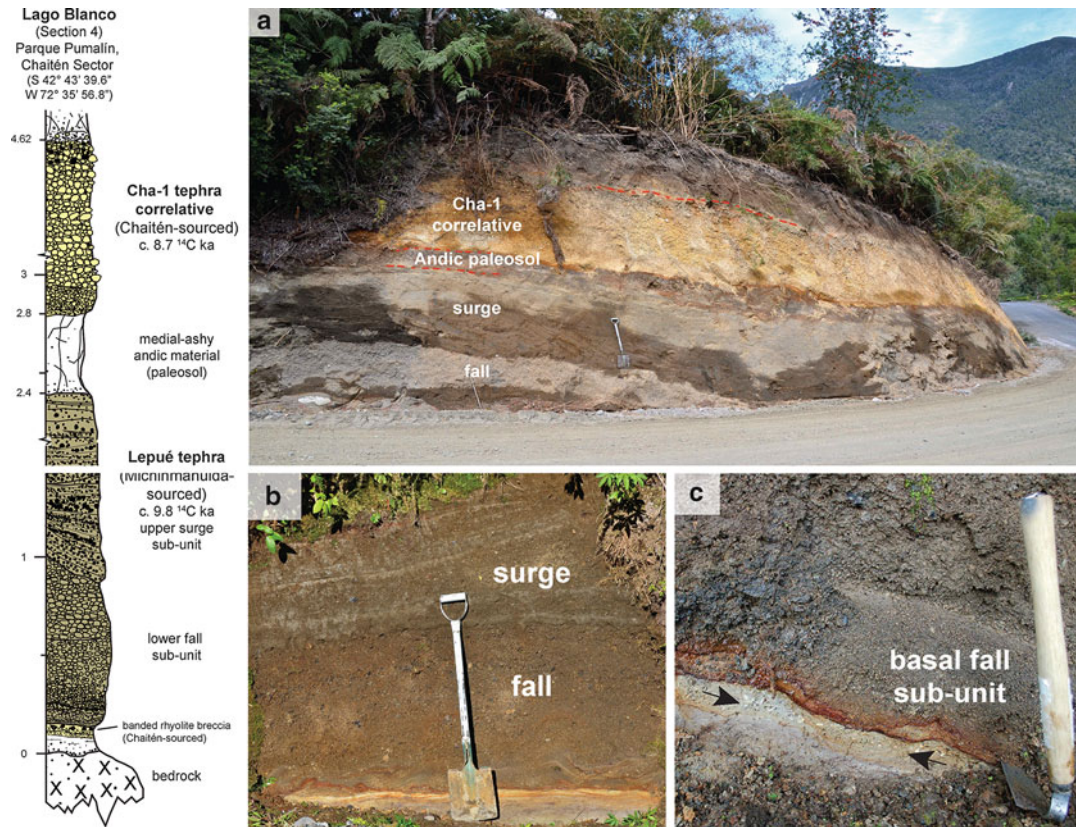


Fig. 2 (a) Road section in the vicinity of Lago Blanco, Chaitén sector (42° S), southern Chile. The stratigraphy at this section reveals (from *top*) a prominent rhyolitic (c. 76 % SiO₂) pumiceous lapilli deposit (Cha-1 correlative) dated at c. 8,700 ¹⁴C year BP and sourced from an ancestral Chaitén volcano, closely overlying a rhyolitic (c. 71 % SiO₂) surge and fall couplet informally named Lepué tephra. This lower rhyolitic eruptive couplet, dated at c. 9,800 ¹⁴C year BP, is sourced from the nearby Michinmahuida Volcanic Complex (MVC). The buried soil horizon (“andic paleosol”) marks the hiatus between the Lepué and Cha-1 eruptions. (b) Low-angle cross-bedding and crosscutting relationship of the surge deposit across its co-eruptive fall deposit, Lepué tephra. (c) The Michinmahuida-sourced eruptive couplet is closely underlain by a widespread and distinctive layer of banded high-Si rhyolite breccia (indicated by *arrows*) that likely represents the products of an explosion of a pre-Cha-1 lava dome (ancestral Chaitén volcano). Such sections are particularly important in terms of recognizing eruptives with different field expression and composition, as well as for unraveling the complex and variable histories of closely situated (adjacent) eruptive centers (Photos: Brent Alloway)

for decades in the aftermath of a paroxysmal eruption (e.g., following the 1991 Pinatubo eruption; Torres et al. 2004). Remobilization of tephra can also be triggered by human activities (Swindles et al. 2013). Such reworked or disseminated tephra-derived constituents, including glass shards, form diachronous rather than isochronous surfaces, and hence their use as stratigraphic tie points is compromised unless remobilization is very localized or near contemporaneous with the primary depositional event. The non-reworked part of a tephra deposit provides an isochron of maximum age (the date of the tephra eruption and primary deposition), but any reworked components are younger (Lowe 2011).

Field correlation methods are increasingly limited as the tephra layers become thinner and finer with increasing distance away from source (e.g., Fig. 5), and the tephtras may become more irregularly distributed (e.g., Turney and Lowe 2001; Lawson et al. 2012). The tephtras typically lose diagnostic physical features (such as internal bedding) in subaerial sequences, and thin, separate beds can become mixed together by soil-forming processes or bioturbation, or by cryoturbation in periodically or perennially frozen landscapes (Sanborne et al. 2006; Lowe and Tonkin 2010;

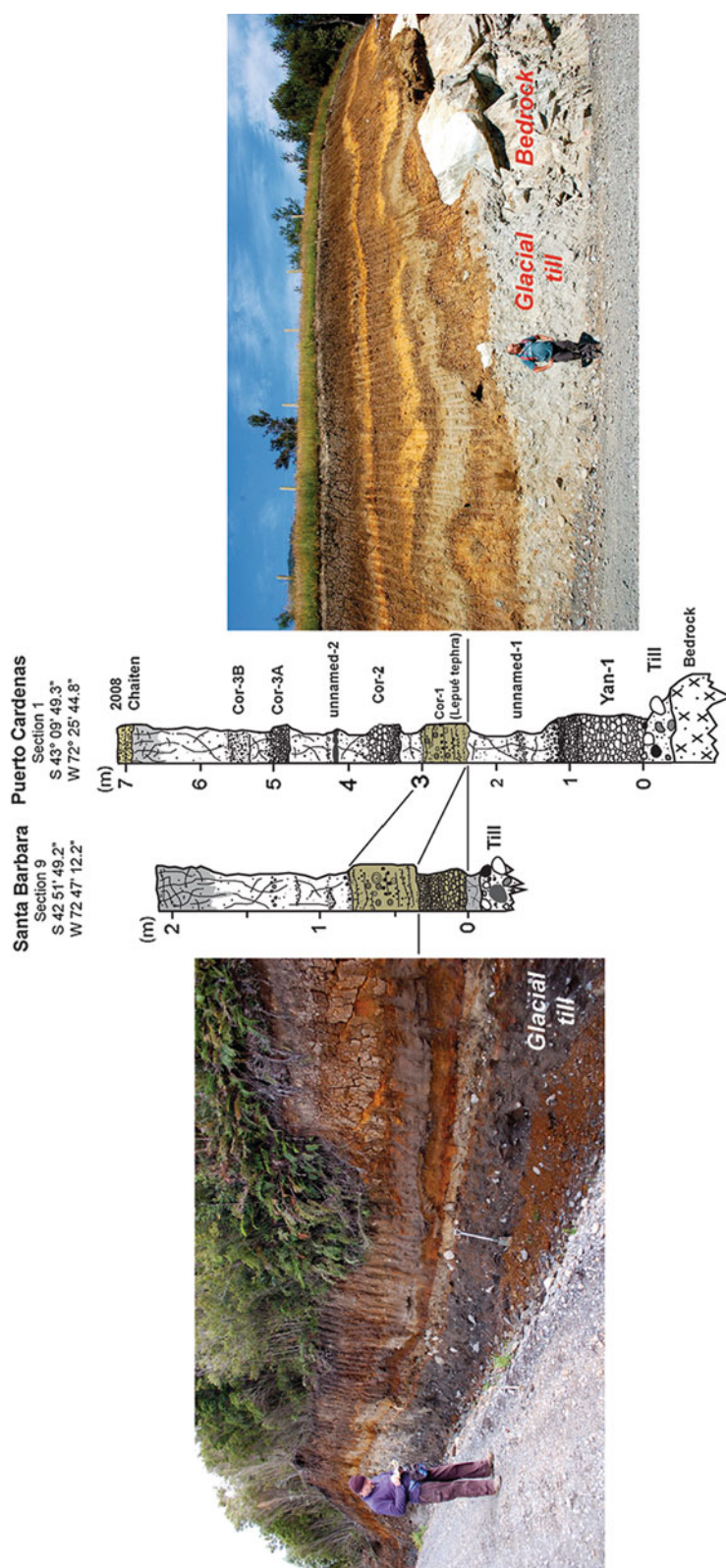


Fig. 3 Stratigraphic columns and corresponding section photos detailing the tephrostratigraphy of deposits at two sites, Santa Barbara and Puerto Cardenas, in the Chaitén sector (42° S) of southern Chile. The tephra notation is from Naranjo and Stern (2004). A key tephra of interest is the prominent decimeter-thick gray tephra layer (Cor-1; now more recently and informally referred to as Lepu tephra) that contains conspicuous accretionary lapilli throughout. This tephra is the product of a large-scale phreatomagmatic eruption sourced from the glaciated Michinmahuida Volcanic Complex (MVC) dated at c. 9,800 ¹⁴C year BP. Tephra from the 2008 eruption of Chaitén volcano occurs on the present-day ground surface. Other strongly pedogenically weathered tephra beds represented within these sections have yet to be geochemically characterized and are probably variably sourced from other nearby volcanoes (Puyuhuapi, Melimoyu, Yanteles, and Corcovado). The tephra sequences at both localities rest on glacial till with a minimum age of c. 14,000 ¹⁴C year BP (Photos: Brent Alloway)

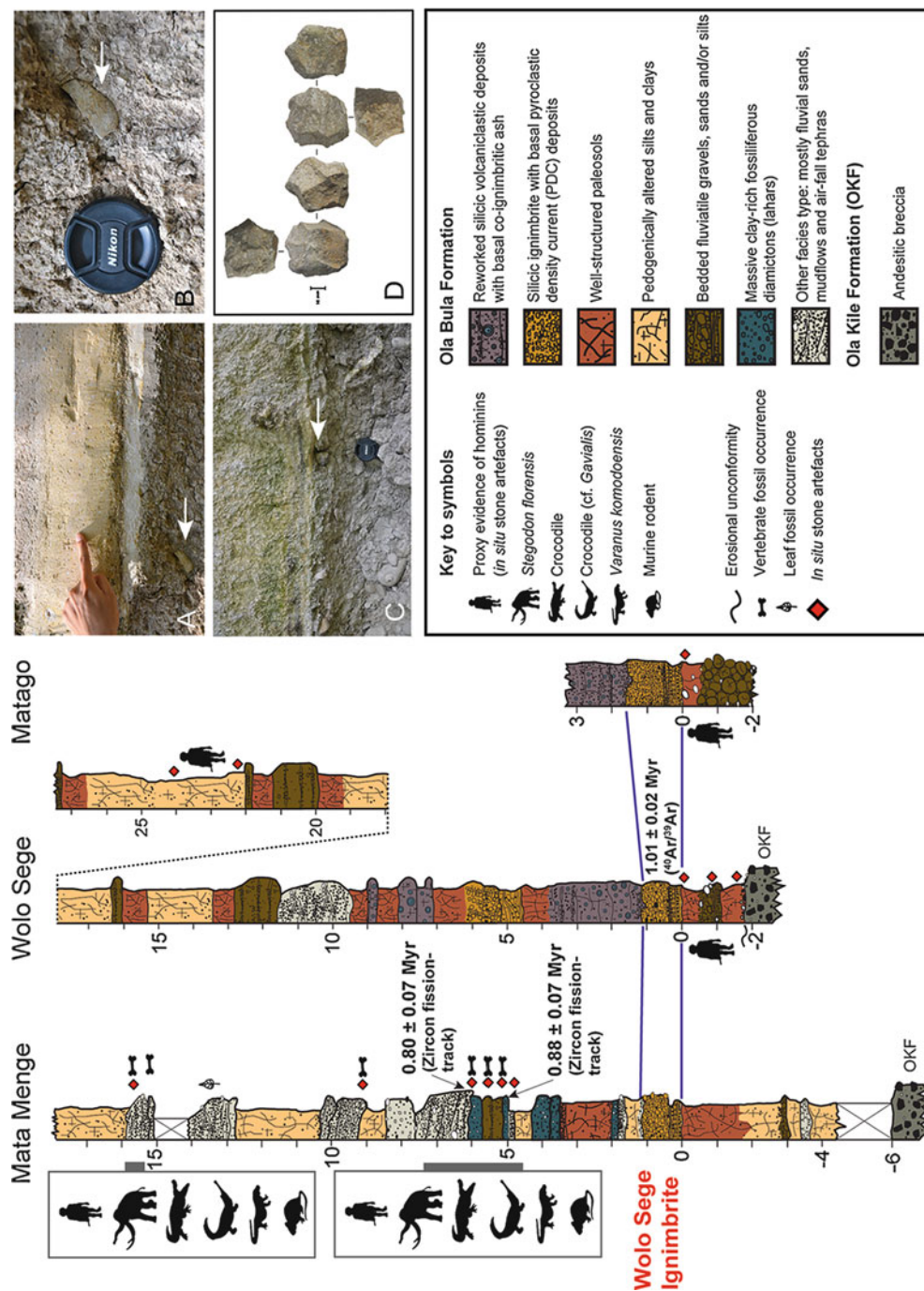


Fig. 4 Stratigraphy associated with hominin stone artifacts and vertebrate fossil remains from the So'a Basin, central Flores, Indonesia (unpublished data of B. V. Alloway, A. Brumm, G. van den Bergh, and R. Setiawan; after O'Sullivan et al. (2001) and Brumm et al. (2010)). The in situ stone artifacts occur immediately beneath a nonwelded (unconsolidated) ignimbrite deposit (Wolo Sege ignimbrite, WSI) that can readily be correlated and distinguished from other enveloping silicic tephra



Fig. 5 A distal occurrence of fine-grained Mazama tephra, 1–2 cm in thickness and composed mainly of glass shards, shows up as the pale “break” (where the person is touching) in an alluvium-soil sequence on the lowermost terrace alongside the North Saskatchewan River in Edmonton, Alberta, Canada. Multiple buried soils formed on intermittent flood deposits are evident in the section, with the high sedimentation (up-building) rate contributing to the rapid burial and preservation of the thin, fine-grained Mazama tephra as an inconspicuous layer. The Mazama tephra, dated at $7,627 \pm 150$ cal. year BP (Zdanowicz et al. 1999), provides a key isochronous time plane (chronostratigraphic marker bed) for Holocene archaeological and paleoenvironmental studies in the United States and southwestern Canada. Located ~1,450 km northeast of its source (Crater Lake, Oregon), the tephra was first identified here by Westgate et al. (1969) (Photo: David Lowe)

Dugmore and Newton 2012). Cores taken from lake sediments and peat bogs potentially provide a reliable means to record thin and/or fine-grained distal tephra layers, or at proximal or medial locations where tephras tend to be thicker and may have more restricted dispersal patterns around source vents – for example, in basaltic volcanic fields (Shane and Hoverd 2002). These lake or bog depositional environments allow thin tephras or glass-shard concentrations (cryptotephras) to be preserved amidst organic-bearing sediments (Fig. 6) (de Fontaine et al. 2007; Smith et al. 2013), notwithstanding potential taphonomic difficulties posed by tephra reworking or dispersion (Lowe 2011; Liu et al. 2014). Marine cores, especially from locations downwind of eruption centers, may also contain detailed records of tephra layers or cryptotephras intercalated with sediments (e.g., Guðmundsdóttir et al. 2012; Abbott et al. 2013; Ponomareva et al. 2013b; Austin et al. 2014).



Fig. 4 (continued) interbeds across the So’a Basin on the basis of its unique depositional architecture as well as its major-element glass-shard composition. The WSI, dated at 1.02 ± 0.02 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ (Brumm et al. 2010), provides important evidence for the presence of hominins on Flores for over 1 million years. (a) The base of WSI at the Wolo Sege section showing distinctive surge-like subunits containing accretionary lapilli and bedding consistent with the density segregation of entrained particles. Note the in situ bifacial flake in the paleosol immediately beneath the base of the WSI (indicated by arrow). (b) Close-up photo of the in situ bifacial flake identified at Wolo Sege. (c) In situ flaked core stone identified at the Matago section on the paleo-ground surface buried by the WSI. (d) Close-up photo showing the detail of the flaked core stone from the Matago section (Photos a–c: Brent Alloway; Photo d: Adam Brumm)

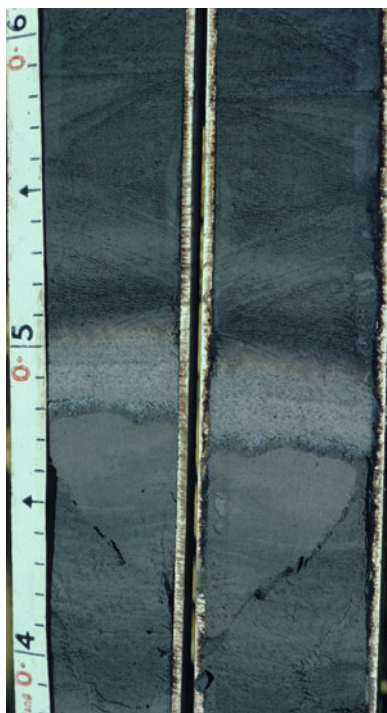


Fig. 6 Close-up of a near-basal part of a lake sediment core from Lake Okoroire, New Zealand, showing 3-cm-thick Rerewhakaaitu tephra, erupted $17,496 \pm 462$ cal. year BP from Mt Tarawera in the Okataina Volcanic Centre (Lowe et al. 2013; see Fig. 8 below). Many tiny *black specks* in the layer represent free biotite crystals diagnostic of this (and some other) tephtras derived from Mt Tarawera. Different sediment colors above and below the tephra reflect a climatically driven change from shrubland/grassland to forest in the region soon after the eruption (Newnham et al. 2003; Alloway et al. 2007). An indistinct uncorrelated tephra lies ~2 cm above the Rerewhakaaitu tephra. Scale marks in centimeters (Photo: David Lowe)

Possible reworking of tephtras (by currents, ice rafting, bioturbation) adds complexity in some cases (Brendryen et al. 2010; Larsen et al. 2014; Todd et al. 2014).

Together with those from lakes and bogs, many of the records of marine tephra deposits can thus document patterns of explosive volcanism in time and space and integrate the stratigraphic interfingering of eruptives from multiple volcanic sources (Shane et al. 2006; Swindles et al. 2011; Ponomareva et al. 2013a, b). Such compilations are often more comprehensive than those obtainable near volcanic centers because of burial or erosion of eruptives at such proximal locations, but an important caveat is that proximal deposits are typically more compositionally variable than distal deposits (e.g., Smith et al. 2005; Shane et al. 2008a). On this basis, distal deposits usually have a more restricted compositional range than otherwise might be generated during a particular eruptive episode.

Distal Tephtras and Cryptotephra Deposits

Submillimeter-scale studies have involved the development of new approaches to enable cryptotephtras, and very thin distal tephtras, to be mapped, albeit discontinuously, across landscapes using a range of methods firstly to *detect* and *isolate* glass-shard or crystal concentrations (e.g., Hall and Pilcher 2002; Gehrels et al. 2006; Swindles et al. 2010; Lane et al. 2014) and secondly to *correlate* them with known (previously characterized) deposits using geochemical analyses of glass shards, melt inclusions (glass) within crystals, or crystals (Matsu'ura et al. 2011; Swindles et al. 2013) as described below. Cryptotephtras have been discovered in peat, lake, marine, aeolian,

or frozen sediments or ice, in deposits in caves or rock shelters, and in soils or paleosols. They (and thin visible tephra) have been detected using ground-penetrating radar, magnetic susceptibility and remanent magnetization, X-radiography, X-ray fluorescence (including use of scanners), spectrophotometry, micro-petrography, enumeration of glass shards, and measurements of total organic carbon and loss on ignition (Turney and Lowe 2001; Gehrels et al. 2008; Lawson et al. 2012). These novel cryptotephra studies, although not without problems and limitations (e.g., Davies et al. 2007; Payne and Gehrels 2010; Swindles et al. 2011), have documented tephra-fall occurrences at submillimeter scales at distances of hundreds to some thousands of kilometers from source, greatly extending known geographical limits (e.g., Payne et al. 2008; Davies et al. 2010, 2012; Balascio et al. 2011). Pyne-O'Donnell et al. (2012) showed that “ultra-distal” cryptotephra derived from Holocene eruptions in Alaska and the Pacific Northwest occur ~7,000 km from source in eastern-most North America and one tephra, the Alaskan White River Ash (eastern lobe, erupted around AD 860), occurs ~16,000 km away in Ireland (Jensen et al. 2014). Lane et al. (2013) identified the c. 75,000-year-old Youngest Toba Tuff tephra as a cryptotephra deposit in Lake Malawi sediments in east Africa, >7,000 km west of the source volcano in Sumatra. Cryptotephra associated with the eruption of the Campanian Ignimbrite in Italy c. 40,000 calendar (cal.) year BP was identified across much of central Europe and the Mediterranean area by Lowe et al. (2012). As noted earlier with regard to visible tephra deposits, cryptotephra studies can help also in elucidating the eruptive history of volcanoes (e.g., Shane et al. 2013).

Ice cores provide detailed and valuable records of volcanism (Davies et al. 2010; Dunbar and Kurbatov 2011; Abbott and Davies 2012; Coulter et al. 2012). Until recently, analytical limitations of geochemical techniques have hindered adequate characterization of ultrafine glass particles (<5 µm) and identification of their eruptive source. Similarly, sulfate records in ice cores may not always act as suitable proxies for the occurrence of tephra or cryptotephra deposits composed of (typically sparse) glass shards in the cores (Davies et al. 2010; Abbott and Davies 2012).

Characterizing Tephra and Cryptotephra in the Laboratory

The characterization, or “fingerprinting,” of mineral and glass components of tephra or cryptotephra can be undertaken using a range of analytical methods (Table 1). Such characterization is almost always carried out in conjunction with lithostratigraphic and chronological criteria to obtain cogent correlations (Alloway et al. 2013).

Ferromagnesian Silicate Mineral Assemblages

A common method is to use a petrographic microscope to identify ferromagnesian or mafic mineralogical assemblages where such minerals are abundant, usually at proximal or medial sites. These minerals can be extracted using a magnetic separator together with nontoxic heavy liquids such as sodium polytungstate. With stratigraphic and age constraints, the relative abundances of ferromagnesian minerals may allow a source volcano to be identified. For example, in the Yukon Territory of Canada, Preece et al. (2000, 2011a) showed that tephra erupted from the Aleutian arc-Alaska Peninsula, so-called Type I beds, had low crystal contents comprising mainly pyroxene (and mainly bubble-wall shards), whereas tephra derived from the Wrangell volcanic field and Hayes volcano, Type II beds, generally had high crystal contents comprising mainly hornblende (and mostly pumiceous shards). In New Zealand, orthopyroxene (mainly hypersthene) is dominant in tephra erupted from the Taupo Volcanic Centre since c. 30,000 cal. year BP, whereas biotite,

Table 1 Analytical methods (excluding geochronology) used to characterize glass or minerals in tephra to facilitate their correlation (after Lowe 2011)

Tephra components and properties	Main methods of analysis ^a
Glass shards^b	
Major and minor elements ^c	Electron microprobe
Trace elements ^c including rare earths	LA- or SN-ICPMS, INAA, SIMS
Sr, Nd, and Pb isotopes	LA-ICPMS, multi-collector NMS
Shard morphology	Optical microscope, SEM
Melt inclusions (glass)	
Major and minor elements	Electron microprobe
Trace elements	SIMS, LA-ICPMS
Ferromagnesian silicate minerals	
Assemblages or marker minerals	Petrographic microscope, XRD
Pyroxenes, amphiboles, olivine, or biotite crystals/phenocrysts	Electron microprobe
Crystal geometry	Optical microscope, SEM
Apatite, zircon	
Apatite or zircon ^d crystals/phenocrysts	Electron microprobe, TIMS-TEA
Crystal geometry	Optical microscope, SEM
Fe-Ti oxides	
Major and minor elements	Electron microprobe
Eruption temperatures and oxygen fugacities	Electron microprobe
Feldspars^d	
Plagioclase, anorthoclase, or sanidine crystals/phenocrysts	Electron microprobe

^aLA- or SN-ICPMS laser ablation or solution nebulization inductively coupled plasma mass spectrometry, INAA instrumental neutron activation analysis, SIMS secondary ionization mass spectrometry (ion probe), NMS nuclide mass spectrometry, SEM scanning electron microscopy, XRD X-ray diffraction, TIMS-TEA thermal ionization mass spectrometry-trace element analysis

^bMay also include glass coats (selvedges) or matrix glass in pumice clasts

^cMajor elements expressed as oxides usually are defined as >1 wt%, minor element oxides as 0.1–1 wt%, and trace elements as <0.1 wt% or <1,000 parts per million (ppm) of the element (not oxides)

^dAnalyses of these minerals generally are less useful for correlating individual tephra

hornblende, cummingtonite, or orthopyroxene predominate in tephra erupted from the Okataina Volcanic Centre over the same period (Lowe et al. 2008).

In some cases an individual tephra can be identified using distinctive, diagnostic marker minerals, such as aegirine and aenigmatite in the Tuhua Tephra that were erupted from peralkaline Mayor Island volcano c. 7,000 cal. year BP in New Zealand. However, the absence of diagnostic minerals does not necessarily negate correlation because minerals such as olivine, biotite, and hypersthene can be dissolved comparatively quickly in some very acid peat bogs (within 700 years; Hodder et al. 1991) or in soil-forming environments (Lowe 1986; Churchman and Lowe 2012). Ferromagnesian minerals and Fe-Ti oxides also tend to be sparse or absent at distal localities, dropping out from proximal or medial ash clouds earlier because of their high density (Juvigné and Porter 1985).

Although of limited application, the crystal geometry (crystal width) of apatite (a phosphate-group mineral) was shown to be useful, along with apatite trace-element data, for differentiating beds in a study of Late Ordovician K-bentonites in the USA by Sell and Samson (2011). Similarly, Donoghue et al. (1991) showed that two distinct crystal geometries of olivine (skeletal, non-skeletal) were useful in correlating some andesitic tephra in New Zealand.

Major-Element Analysis of Glass Shards, Melt Inclusions, and Minerals

The electron microprobe enables a range of tephra components to be analyzed for major elements on a grain-by-grain basis: individual glass shards, glassy coatings on crystals, melt inclusions (glass preserved within crystals including quartz, pyroxenes, amphiboles), pumice fragments, and loose crystals or phenocrysts including various ferromagnesian silicate minerals, apatite, zircon, and Fe-Ti oxides such as titanomagnetite (Table 1). The main advantage of the microprobe and other single-grain techniques is that they allow mixed or heterogeneous populations to be identified. Because volcanic glass is amorphous, its analysis by microprobe needs especially careful sample preparation and mounting, the use of appropriate standards, and optimum probe-operating conditions to derive accurate and robust data (Kuehn et al. 2011; Hall and Hayward 2014; Pearce et al. 2014; Suzuki et al. 2014).

Usually a defocused (e.g., 10–20 μm) or rastered beam is deployed to minimize the mobilization of Na, although protocols that use narrower beam diameters (3–5 μm) without loss of Na have been recently developed for analyzing fine-grained glass shards, as occur in distal or ultra-distal tephtras or cryptotephtras or glasses with microlites (Hayward 2012; Pyne-O'Donnell et al. 2012; Hall and Hayward 2014). Glass microprobe analyses are usually normalized (summed to 100 %, most, but not all, of the deficit being attributable to water) to enable useful comparisons of analyses (Shane 2000; Lowe 2011; Westgate et al. 2013a). Using stratigraphic or age constraints, and usually also a knowledge of geochemical affinities of potential source rocks/deposits and spatial distribution patterns, the microprobe analysis of glass may allow tephra source volcanoes to be identified, and individual eruptives may also be correlated in some cases where compositions through time have changed from one eruptive event to the next. Complexities arise where glass analyses show heterogeneity, a consequence potentially of (i) mingling or mixing of separate batches of magmas that were tapped simultaneously or sequentially as eruptions proceeded (e.g., Tryon et al. 2010; Turner et al. 2011b), (ii) major-element evolution by fractional crystallization or crustal assimilation (Bogaard and Schminke 1985; Ukstins Peate et al. 2008; Óladóttir et al. 2012), (iii) blending of thin tephtras in soil-forming or cryogenic environments (Lowe 1986; Eden et al. 2001; Dugmore and Newton 2012), or (iv) postdepositional dissemination of glass shards in peat, lake, or marine sediments (Gehrels et al. 2006; Allan et al. 2008; Abbott et al. 2013). Heterogeneity arising from magmatic or volcanic eruption processes accompanied by changes in wind direction warns of the difficulty of characterizing (thus fingerprinting) tephra beds using a limited set of distal samples from restricted dispersal sectors (Shane et al. 2008a). Another problem can arise with analyses of melt inclusions where these do not reflect the full compositional range of glass shards or matrix glass (e.g., Shane et al. 2008b; Chesner and Luhr 2010; Allan et al. 2013), or they show a pattern different from that associated with matrix glass analyses (e.g., Kilgour et al. 2013). Once recognized, such compositional variability can enhance correlation by providing additional fingerprinting criteria, but sampling from the full spatial and temporal range of deposits of an eruptive sequence is required (Alloway et al. 2013).

The correlation of andesitic or basaltic tephtras using glass chemistry generally can be complicated for various reasons including the multiplicity of units, the paucity of suitable glass for microprobing (shards may contain micro-inclusions and can be highly vesicular), susceptibility of glass to weathering, and wide compositional ranges and potential heterogeneity as noted previously (Moebis et al. 2011; Shane and Zawalna-Geer 2011; Óladóttir et al. 2012). Platz et al. (2007) provided a procedure to evaluate glass compositional variability arising from the inadvertent microanalysis of plagioclase microlites in shards using a wide beam, but the recent use of narrower beam diameters is helping to obviate this problem (Hayward 2012; Pearce et al. 2014).

Analyses by microprobe of ferromagnesian silicate minerals, such as biotite (Shane et al. 2003; Smith et al. 2011) and cummingtonite (Matsu'ura et al. 2012), apatite (a phosphate-group mineral) (Sell and Samson 2011), and Fe-Ti oxides such as titanomagnetite and ilmenite (Shane 1998; Preece et al. 2011b; Marcaida et al. 2014), have also been used for tephra fingerprinting. In some cases, and after taking into account compositional zoning within crystals, trace elements such as Mg, Cl, Mn, Fe, Ce, and Y identified in apatite crystals and phenocrysts provide a means of distinguishing or matching tephras (Sell and Samson 2011). The eruption temperature and oxygen fugacity (oxidation state of magma) of rhyolitic tephras – estimated using single-grain EMPA of Fe-Ti oxide pairs of titanomagnetite and ilmenite – provide another way to correlate tephras and, in some cases, magma batches within an eruptive sequence (Smith et al. 2005; Preece et al. 2011b; Marcaida et al. 2014).

Trace-Element and Isotope Analysis of Glass

Although the microprobe is now the key analytical tool for undertaking major-element analyses of glass, tephras or cryptotephras cannot always be distinguishable uniquely by major-element data alone. In these cases, other analytical methods are needed (Westgate et al. 2013c). Trace-element analyses of glass separates from tephra or cryptotephra deposits offer a greater range of elements for use in correlation/provenance studies and may also provide additional information on volcanic petrogenesis. In the last decade, trace-element techniques have become more common, the most widely available being laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (e.g., Albert et al. 2012; Ponomareva et al. 2013a; Sulpizio et al. 2013) (Table 1). Around 150 individual glass shards can be analyzed for about 30 trace elements in 1 day using LA-ICPMS (Pearce et al. 2011). Comprehensive studies using this method were undertaken on Pleistocene tephras in northern New Zealand (Pearce et al. 2008b) and in marine cores from Ocean Drilling Project (ODP) Site 1123 (Allan et al. 2008). The most useful elements for correlating and distinguishing between the ODP Site 1123 tephras were found to be the abundances of Rb, Ba, Sr, Y, Zr, Hf, Mg, Mn, and Ti and trace-element ratios including Rb/Sr, Ba/Sr, Zr/Y, Y/Th, Ba/Th, and Rb/Sm. Using trace-element data for glass shards, Allan et al. (2008) demonstrated that (i) tephras with similar major-element compositions (e.g., Kawakawa tephra vs. Omataroa tephra) were easily distinguishable (Fig. 7), and (ii) two previously unidentified repeated sections of ODP cores 1123A (~4.5 m thick) and 1123C (~7.9 m thick) were recognized (Allan et al. 2008). As with the microprobe, there is a possibility of microlites affecting trace-element characterizations of individual shards via LA-ICPMS and so anomalous assays need to be evaluated carefully (Abbott et al. 2013).

Analyses of isotopes of Sr, Nd, and Pb in glass (or pumices) have been utilized in several studies to help determine tephra source volcanoes (e.g., Roulleau et al. 2009; Westgate et al. 2008, 2011; Giaccio et al. 2013).

Comparing Compositional Data Using Graphical, Numerical, and Statistical Methods

Major- or trace-element datasets obtained from analyses of glass or minerals may be displayed and compared, and hence compositional variability evaluated, using various methods: graphical (e.g., bivariate or trivariate plots), numerical (e.g., similarity coefficients), or statistical (e.g., statistical distance measure, dendrograms, discriminant function analysis, principal components analysis) (Pearce et al. 2008a; Bourne et al. 2010; Lowe 2011; Sell and Samson 2011). In many cases, the bivariate plots alone can provide sufficient guidance to enable anomalous data points to be identified (and possibly explained using compositional databases for comparison), and potential correlations or otherwise established with reasonable likelihood, especially where multiple criteria provide

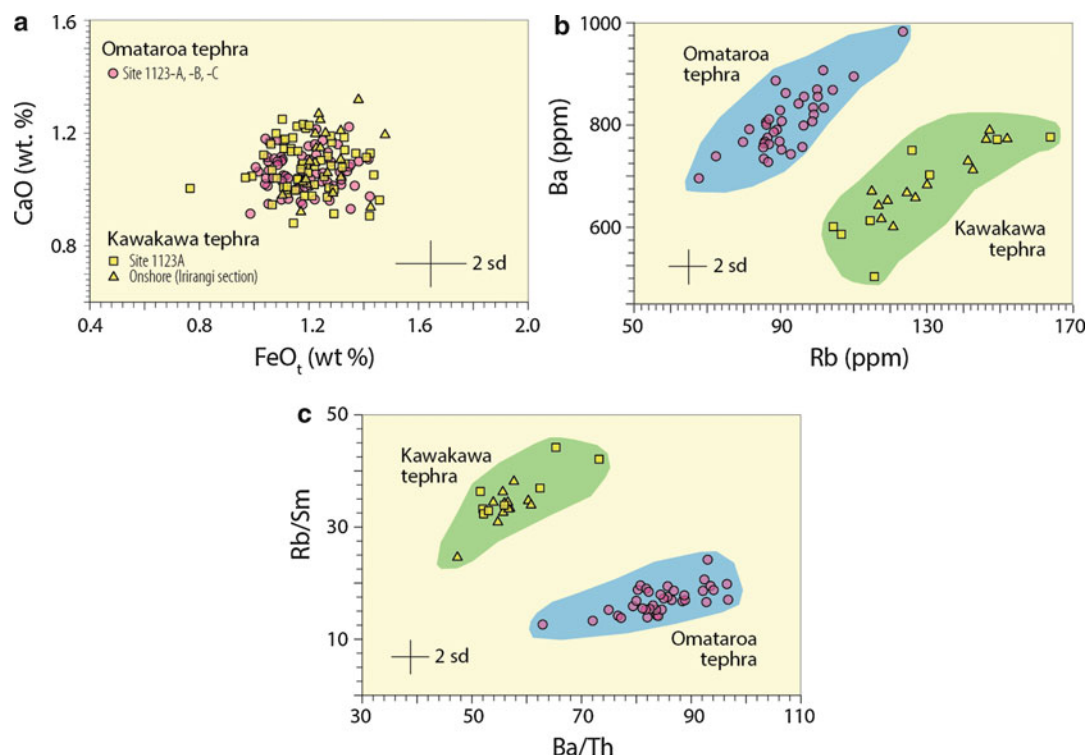


Fig. 7 Bivariate plots for some major and trace elements derived from analyses of individual glass shards from two New Zealand tephra, Omataroa (c. 31,600 cal. year BP, erupted from Okataina Volcanic Centre) and Kawakawa (c. 25,400 cal. year BP, erupted from Taupo Volcanic Centre), identified in marine cores *A*, *B*, and *C* from ODP Site 1123 about 1,200 km east of New Zealand (Modified after Allan et al. 2008, p. 2351, with permission of Elsevier). (a) CaO versus FeO_t (total iron expressed as FeO) derived by electron microprobe. Glass analyses from an onshore occurrence of Kawakawa tephra (at Irirangi) are also shown for comparison. The plot shows that the analyses of marine and onshore samples of Kawakawa tephra are identical and that Kawakawa and Omataroa tephra cannot be distinguished using these two oxides alone. In contrast, trace-element concentrations (in ppm), derived by LA-ICPMS, in (b) and (c), show that the tephra are distinctly different with respect to their elements/element ratios and hence can be readily distinguished

independent support, such as concordance of glass major- and trace-element data together with Fe-Ti oxide data (e.g., see Preece et al. 1999, 2011b). In other situations, however, statistical methods such as principal components analysis can allow units to be distinguished objectively on the basis of multiple oxides or elements (not just two or three) analyzed from glass shards or crystals (e.g., Tryon et al. 2010; Chiasera and Cortés 2011; Sell and Samson 2011).

Dating Tephra (Tephrochronometry)

Tephra may be dated directly using primary minerals (e.g., zircon, hornblende, K-feldspars, biotite, quartz) or glass from within the tephra layer, or indirectly on either enclosing or encapsulated material, using a range of methods including radiometric, incremental (e.g., varves, layering in ice), and age equivalence (Table 2) (Svensson et al. 2008; Alloway et al. 2013; Zalasiewicz et al. 2013). These ages can then be transferred from one site to another where the tephra is recognized using the lithostratigraphic and compositional-based methods described above. Only the main radiometric methods, and age modeling, are touched on here.

Table 2 Methods used for dating tephtras directly or indirectly (after Lowe 2011)

Main method	Applications
Radiometric	Radiocarbon dating (radiometric/beta counting, AMS) ^a Fission-track dating of zircon or glass-ITPFT or glass-DCFT dating Argon isotopes (K/Ar, Ar/Ar including SCLP/F, LIH) Luminescence dating (TL, OSL, IRSL, pIR-IRSL) U-series including (U-Th)/He, U-Pb, and ²³⁸ U/ ²³⁰ Th zircon dating (SIMS/TIMS, SHRIMP, LA-ICPMS) Electron spin resonance ²¹⁰ Pb, ¹³⁷ Cs, ³ He and ²¹ Ne surface exposure dating
Incremental	Dendrochronology, varve chronology, layering in ice cores (ice sheets/caps, glaciers)
Age equivalence	Magnetopolarity, paleomagnetic secular variation, astronomical (orbital) tuning, correlation with marine oxygen isotope stages, climatostratigraphy, biostratigraphy, palynostratigraphy, paleopedology
Age modeling	Various age-depth methods including Bayesian flexible depositional modeling and wiggle matching, spline-fit modeling
Relative	Obsidian hydration dating, amino acid racemization
Historical	Eyewitness accounts or observations (e.g., via remote sensing)

^aAMS accelerator mass spectrometry, ITPFT isothermal-plateau fission track, DCFT diameter-corrected fission track, SCLP/F single-crystal laser probe or fusion, LIH laser incremental heating, TL thermoluminescence, OSL optically stimulated luminescence, IRSL infrared stimulated luminescence, pIR-IRSL post infrared-infrared stimulated luminescence, SIMS secondary ionization mass spectrometry, TIMS thermal ionization mass spectrometry, SHRIMP sensitive high-resolution ion microprobe, LA-ICPMS laser ablation inductively coupled plasma mass spectrometry

For tephtras erupted within the past c. 60,000 calendar years, the radiocarbon (¹⁴C) technique (e.g., Hogg et al. 2007) remains the most important method for developing calibrated age models. In recent years, the advantages of using pollen concentrates and terrestrial plant macrofossils (e.g., leaves, twigs), rather than bulk organic samples, as reliable dating materials via AMS have been demonstrated (Newnham et al. 2007; Staff et al. 2011). Together with dendrochronological wiggle-matching methods (Hogg et al. 2012; Yin et al. 2012), Bayesian flexible depositional age modeling has added a revolutionary aspect to the construction of enhanced and more precise chronologies in tephrochronology involving ¹⁴C and other dating methods (Blockley et al. 2008; Smith et al. 2013). Lowe et al. (2013) dated late Quaternary tephtras in New Zealand by modeling ¹⁴C age data using two Bayesian-based programs, *Bacon* (Blaauw and Christen 2011) and OxCal's *P_Sequence* function (Bronk Ramsey 2009), and the IntCal09 dataset (Fig. 8). Lohne et al. (2013) also used *P_Sequence* and IntCal09 to obtain high-precision ages of 12,066 ± 42 and 10,210 ± 35 cal. year BP (±1σ) for the Vedde and Saksunarvatn tephtras, respectively, from sediments in Kråkenes Lake, Norway. Similarly, the AT tephtra of Japan was dated to 30,009 ± 189 cal. year BP (95 % probability) using *P_Sequence* modeling of ¹⁴C data and varves (Smith et al. 2013). Vandergoes et al. (2013) used OxCal's *Tau_Boundary* function, also Bayesian, to precisely date the Kawakawa/Oruanui tephtra of New Zealand to 25,358 ± 162 cal. year BP (95 % probability).

Another key advance in tephrochronology has been the development of the isothermal-plateau fission-track dating method (ITPFT) for glass (Westgate 1989; Alloway et al. 2004b, 2013; Westgate et al. 2013b). ITPFT and the diameter-corrected fission-track method (Sandhu and Westgate 1995) have enabled ages to be obtained on many distal vitric-rich tephtras that previously were unable to be dated because of low abundance of dateable mineral constituents, fine grain size, and the presence of detrital grains. Examples of such applications include dating Quaternary glacioeustatic sedimentary cycles in the Wanganui Basin (Alloway et al. 1993; Pillans et al. 2005) and dating initial loess deposition in Alaska at ~3 million years ago (Westgate et al. 1990). The glass-FT techniques have

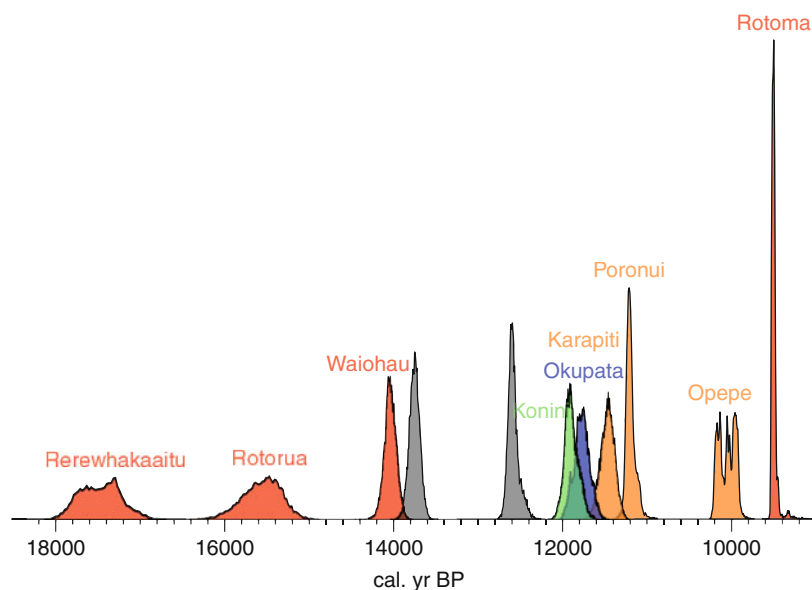


Fig. 8 Bayesian-derived age models (95 % probability) for nine late Quaternary tephras in New Zealand (From Lowe et al. 2013, p. 179, with permission of Elsevier). Probability plots are colored according to tephra source volcanoes: *red*, Okataina; *orange*, Taupo; *green*, Taranaki; and *blue*, Tongariro. *Gray* plots show the start and end ages of the lateglacial cool episode, designated climate event NZce-3 by Barrell et al. (2013), in part constrained chronologically by the ages on the adjacent tephras

been used, for example, also to test chronologies based on alternative methods (such as magnetic polarity and astronomical tuning) for marine tephra sequences (Alloway et al. 2005; Allan et al. 2008) and for fossiliferous alluvial and lacustrine sediments in Beringia (Preece et al. 2011b; Westgate et al. 2013a).

Where suitable minerals are available (e.g., sanidine, biotite, leucite, anorthoclase), the $^{40}\text{Ar}/^{39}\text{Ar}$ method has been useful, such as dating the Laacher See tephra in Germany (Bogaard 1995), the ultra-distal to distal deposits of the Youngest Toba Tuff tephra of Indonesia (Westgate et al. 1998; Storey et al. 2012), a widespread Holocene tephra erupted from Ulleungdo stratovolcano in South Korea (Smith et al. 2013), a 400,000-year-old sequence of eruptives from Nemrut volcano preserved in Lake Van, eastern Anatolia in Turkey (Sumita and Schminke 2013), and the distal tephras preserved in lacustrine and fluvial sediments of intermontane basins of central Italy (Giaccio et al. 2013). A relatively new method for dating proximal pyroclastic deposits, previously applied to petrologic studies, is the use of U-Pb analyses to date zircons (Schmitt 2006; Dickinson et al. 2010; Wilson et al. 2010). Luminescence and (U-Th)/He dating methods are also being applied systematically to tephras (Danišík et al. 2012; Biswas et al. 2013).

A trend in dating lake sediment sequences containing tephras or cryptotephra is to apply multiple methods, as exemplified by Staff et al. (2013) and Sirocko et al. (2013).

Conclusions

Tephrochronology is the use of primary tephra or cryptotephra as isochrons to link and synchronize geological, paleoenvironmental, or archaeological sequences or events, or soils, and, uniquely, to transfer relative or numerical ages to them using stratigraphic information and mineralogical and geochemical compositional data, especially from individual glass-shard analyses, obtained for the

tephras/cryptotephras. To function therefore as an age-equivalent correlation and chronostratigraphic dating tool, tephrochronology can be undertaken in three steps: (i) mapping and describing tephras and determining their stratigraphic relationships, (ii) characterizing tephras or cryptotephras in the laboratory, and (iii) dating them using a wide range of geochronological methods. Tephrochronology is also an important tool in volcanology, informing studies on volcanic petrology, volcano eruption histories and hazards, and volcano-climate forcing. Although limitations and problems remain, multidisciplinary applications of tephrochronology continue to grow markedly (e.g., Alloway et al. 2013; Lane et al. 2014).

Acknowledgments

We thank editors Jeroen Thompson and Jack Rink for inviting us to write this entry and for their suggestions, reviewer Vera Ponomareva for her helpful comments, Megan Balks and Adam Brumm for providing photographs, and Chris Hayward and John Westgate for furnishing preprints. Elsevier kindly allowed us to use previously published material (Figs. 7 and 8). The entry was funded in part by the New Zealand Marsden Fund (project 10-UOW-056 to DJL entitled “New views from old soils”), administered by the Royal Society of New Zealand, and it is an output also of the INTREPID Tephra-II project (INQUA project 1307s) “Enhancing tephrochronology as a global research tool through improved fingerprinting and correlation techniques and uncertainty modelling (phase II),” an initiative of the International Focus Group on Tephrochronology and Volcanism (INTAV) supported by the Stratigraphy and Chronology Commission of the International Union for Quaternary Research (INQUA).

Cross-References

- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Dendrochronology, Volcanic Eruptions](#)
- ▶ [Fission Track Dating and Thermochronology](#)
- ▶ [Ice Cores](#)
- ▶ [Luminescence Dating \(Dose Rate\)](#)
- ▶ [Luminescence, Volcanic Rocks](#)
- ▶ [Magnetostatigraphic Dating](#)
- ▶ [Marine Isotope Stratigraphy](#)
- ▶ [Paleosol](#)
- ▶ [Peat \(14C\)](#)
- ▶ [Plant Material \(14C\)](#)
- ▶ [Uranium-Lead, Zircon](#)
- ▶ [U-Th: He Dating](#)
- ▶ [Volcanic Glass \(Fission Track\)](#)

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Tephrochronology

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Synonyms

[Chronostratigraphy](#); [Stratigraphic correlation using tephra](#); [Tephrostratigraphy](#)

Definitions

Tephra. All the explosively erupted, unconsolidated pyroclastic products of a volcanic eruption.

Cryptotephra. Tephra-derived glass-shard and/or crystal concentration preserved in sediments or soils/paleosols but not visible as a layer to the naked eye.

Tephrostratigraphy. Study of sequences of tephra layers or cryptotephra (and associated deposits) and their lithologies, spatial distribution, stratigraphic relationships, and relative and numerical ages. Involves defining, describing, characterizing, and dating tephra layers or cryptotephra deposits in the field and laboratory as a basis for their correlation.

Tephrochronometry. Obtaining a numerical age or calendrical date for a tephra or cryptotephra deposit.

Tephrochronology sensu stricto. The use of primary tephra layers or cryptotephra as isochrons to connect and synchronize depositional sequences, or soils, and to transfer relative or numerical ages to the sequences or soils using lithostratigraphic, compositional, and other data pertaining to the tephra/cryptotephra.

Tephrochronology sensu lato. All aspects of tephra/cryptotephra studies and their application.

Introduction and Definitions

Tephra are the explosively erupted, unconsolidated pyroclastic (fragmental) products of a volcanic eruption (Greek *tephra*, “ashes”) (Lowe 2011). Typically they comprise volcanic glass (including shards, pumice, and scoriae or cinders), rock (lithic) fragments, and crystals (mineral grains), which are erupted through the atmosphere and deposited on the land, the seafloor, or ice caps relatively quickly – usually in a matter of hours or days according to eruption duration (Lowe 2011; Stevenson et al. 2012). A tephra layer deposited from a powerful eruption, and not reworked, consequently forms a widespread, thin blanket on the surface of the Earth that has effectively the same age – an isochron – wherever it occurs. The term “tephra” encompasses all grain sizes: ash (grains <2 mm in diameter), lapilli (64 to 2 mm), or blocks (angular) or bombs (rounded) (>64 mm) (White and Houghton 2006). Diminutive, distal tephra that are not visible as layers in the field are called cryptotephra (Greek *kryptein*, “to hide”). Cryptotephra comprise concentrations of ash-sized glass

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shards or crystals, or both, usually $<150\text{ }\mu\text{m}$ in diameter, preserved in sediments (including ice), in cave deposits, or in soils or paleosols (Lowe 2011; Lane et al. 2014).

Tephrochronology may be defined as the use of primary tephra layers or cryptotephra deposits as isochronous beds to connect and synchronize depositional sequences and to transfer relative or numerical ages (or dates) to such sequences using stratigraphic information together with lithological, compositional, and geochronological data obtained for the tephra or cryptotephra. Tephrochronology is thus a method for correlating and dating geological, paleoecological, paleoclimatic, or archaeological sequences or events, or soils, using characterized tephra or cryptotephra as chronostratigraphic marker beds (Alloway et al. 2013).

Tephrochronology is undertaken typically in three steps. Firstly, tephra deposits are correlated from place to place in the field using their lithostratigraphic and relative age relationships along with intrinsic physical properties, associations with other deposits, and spatial distribution, i.e., tephrostratigraphy (Fig. 1). Fieldwork is carried out at a range of scales because tephra deposits become thinner, and constituent components become smaller, from proximal to distal locations. A potential complication is tephra remobilization, which is discussed later. Secondly, the components of the deposits are characterized or “fingerprinted” using mineralogical or geochemical analytical methods, often both, in the laboratory to aid their correlation. Such laboratory characterization is essential in cryptotephra studies. Thirdly, when a numerical age or date for a tephra or cryptotephra deposit is obtained, i.e., tephrochronometry, that age or date can be transferred from

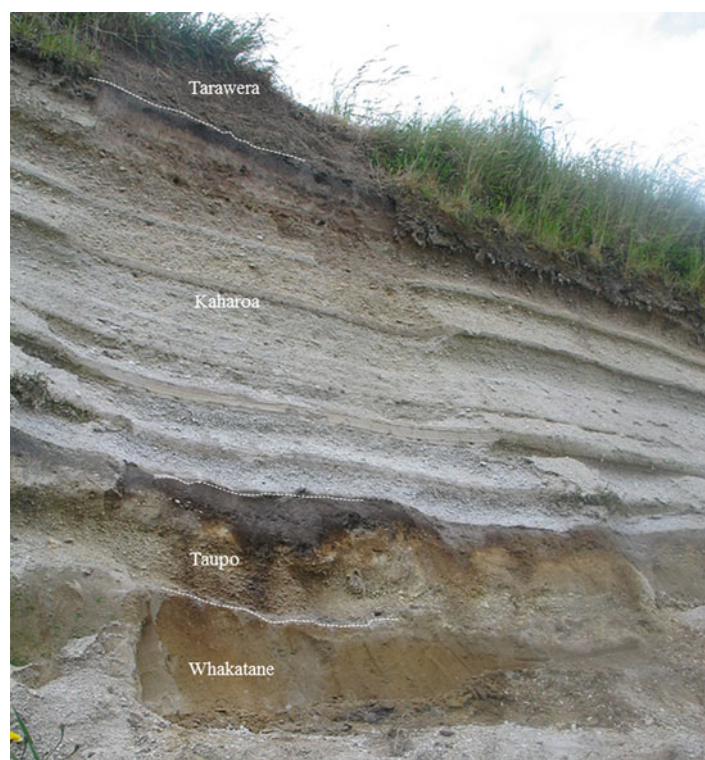


Fig. 1 Stratigraphic sequence of four Holocene tephra deposits of ash and lapilli grade, and buried soil horizons, near Mt Tarawera, New Zealand. Exposure is $\sim 2\text{ m}$ high. From *top*, Tarawera tephra (mainly Rotomahana Mud member) (erupted 10 June 1886); shower-bedded Kaharoa tephra ($\text{AD } 1314 \pm 12$), characterized by abundant biotite; Taupo tephra ($\text{AD } 232 \pm 10$) (note that the *gray* and *very dark-brown* soil horizons evident in the *upper part* of the nonwelded Taupo deposit, Taupo ignimbrite, are the result of podzolization, an acidic soil-leaching process that occurred here prior to the soil's burial by the Kaharoa eruptives); and Whakatane tephra ($5,526 \pm 145\text{ cal. year BP}$) (Ages from Lowe et al. 2013) (Photo: Megan Balks)

one site to the next by comparing the compositional characteristics or “fingerprints” of its components with those of equivalent deposits elsewhere. These three steps – (i) mapping tephras and determining their lithostratigraphic relationships, (ii) characterizing tephras/cryptotephras in the laboratory, and (iii) dating them – enable tephrochronology to function as a unique stratigraphic and geoscientific dating tool and are described below in detail after a subsection on volcanological applications.

Volcanological Applications of Tephrochronology

As well as providing isochrons for geological, archaeological, and paleoenvironmental applications, tephrochronological studies involving mapping, characterization, and dating are critical for developing a comprehensive record of past explosive eruptions and recurrence rates from which time-space relationships of volcanism can be established and volcanic hazards evaluated (e.g., Óladóttir et al. 2008; Kuehn and Negrini 2010). Knowledge of the distribution and thickness relationships of tephra or cryptotephra deposits enables magma volumes to be calculated (Wilson et al. 2009; Ponomareva et al. 2013a). Near to volcanic centers, deposits may include lavas as well as an array of different types of pyroclastic deposits (fall, surge, flow and density current, and explosion breccias; Fig. 2), and detailed studies of their stratigraphic intercalation and physical, mineralogical, and geochemical properties provide insight into volcanic history and petrogenesis (e.g., Ponomareva et al. 2004; Smith et al. 2005; Turner et al. 2011a; Cioni et al. 2014). Information about the release of volatiles into the atmosphere and associated climatic impacts can also be gleaned from studies on tephras (e.g., Zdanowicz et al. 1999; Alloway et al. 2013; Sigl et al. 2013).

Mapping and Correlating Tephras

The most successful approaches in the field include the so-called hand-over-hand method whereby relatively thick sequences of tephras, typically meter to decimeter scale, at proximal or medial locations, are documented and traced from one outcrop or section to the next using distinctive physical properties in combination with their stratigraphic associations (Fig. 3). Physical properties include color, bedding characteristics, or particle-specific features such as pumice/scoria, lithic, and crystal componentry, the presence of accretionary lapilli, or marker mineral grains (crystals) such as biotite identifiable via a hand lens. Distinctive marker beds provide a useful stratigraphic starting point in unraveling the complexities of geological sequences seen in road cuttings or natural exposures, and detailed lithostratigraphic columns are constructed to provide the basis essential for correlating from one site to the next (Fig. 3). The nature of buried soil horizons, loess, or other deposits associated with tephra layers, including (for example) fossils or other attendant paleoecological information such as pollen assemblages (e.g., Newnham and Lowe 1999; Housley et al. 2013; Westgate et al. 2013a) or archaeological relationships (Feibel 1999; Mullen 2012; Riede and Thastrup 2013), may provide additional contextual information helpful for affecting correlation (Fig. 4). High-resolution tephrostratigraphic records in Iceland were constructed by Streeter and Dugmore (2013) using digital photography to obtain thousands of stratigraphic measurements of multiple tephra layers intercalated with sediments at a resolution of 1 mm.

One potential difficulty in tephrostratigraphy arises where tephra remobilization has occurred or where glass shards or crystals have been disseminated or dispersed in sediments or soils, and hence, primary isochron positions are not clear (Alloway et al. 2004a; Pyne-O'Donnell 2011; Housley et al. 2012). Remobilization of tephra resulting from widespread landscape instability in combination with climatic factors (e.g., Manville and Wilson 2004) can remobilize large volumes of tephra

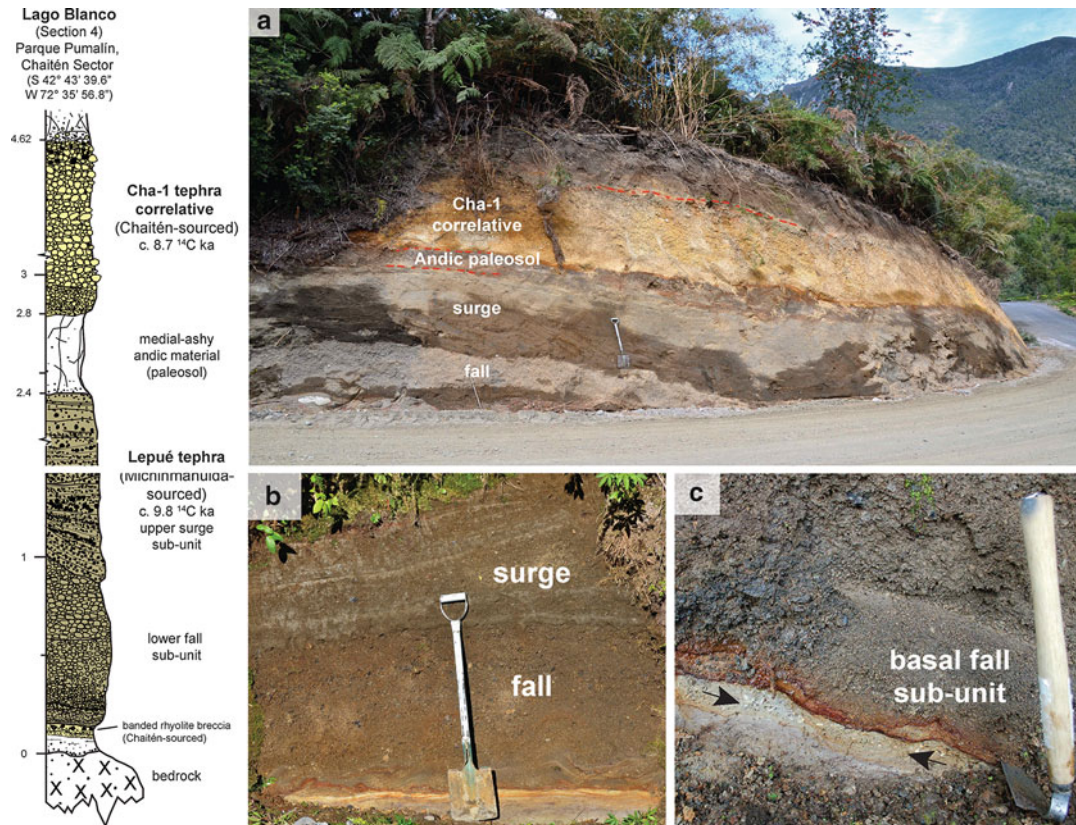


Fig. 2 (a) Road section in the vicinity of Lago Blanco, Chaitén sector (42°S), southern Chile. The stratigraphy at this section reveals (from *top*) a prominent rhyolitic (c. 76 % SiO₂) pumiceous lapilli deposit (Cha-1 correlative) dated at c. 8,700 ¹⁴C year BP and sourced from an ancestral Chaitén volcano, closely overlying a rhyolitic (c. 71 % SiO₂) surge and fall couplet informally named Lepué tephra. This lower rhyolitic eruptive couplet, dated at c. 9,800 ¹⁴C year BP, is sourced from the nearby Michinmahuida Volcanic Complex (MVC). The buried soil horizon (“andic paleosol”) marks the hiatus between the Lepué and Cha-1 eruptions. (b) Low-angle cross-bedding and crosscutting relationship of the surge deposit across its co-eruptive fall deposit, Lepué tephra. (c) The Michinmahuida-sourced eruptive couplet is closely underlain by a widespread and distinctive layer of banded high-Si rhyolite breccia (indicated by *arrows*) that likely represents the products of an explosion of a pre-Cha-1 lava dome (ancestral Chaitén volcano). Such sections are particularly important in terms of recognizing eruptives with different field expression and composition, as well as for unraveling the complex and variable histories of closely situated (adjacent) eruptive centers (Photos: Brent Alloway)

for decades in the aftermath of a paroxysmal eruption (e.g., following the 1991 Pinatubo eruption; Torres et al. 2004). Remobilization of tephra can also be triggered by human activities (Swindles et al. 2013). Such reworked or disseminated tephra-derived constituents, including glass shards, form diachronous rather than isochronous surfaces, and hence, their use as stratigraphic tie points is compromised unless remobilization is very localized or near contemporaneous with the primary depositional event. The non-reworked part of a tephra deposit provides an isochron of maximum age (the date of the tephra eruption and primary deposition), but any reworked components are younger (Lowe 2011).

Field correlation methods are increasingly limited as the tephra layers become thinner and finer with increasing distance away from source (e.g., Fig. 5), and the tephtras may become more irregularly distributed (e.g., Turney and Lowe 2001; Lawson et al. 2012). The tephtras typically lose diagnostic physical features (such as internal bedding) in subaerial sequences, and thin, separate beds can become mixed together by soil-forming processes including bioturbation or by cryoturbation in periodically or perennially frozen landscapes (Sanborne et al. 2006; Lowe and

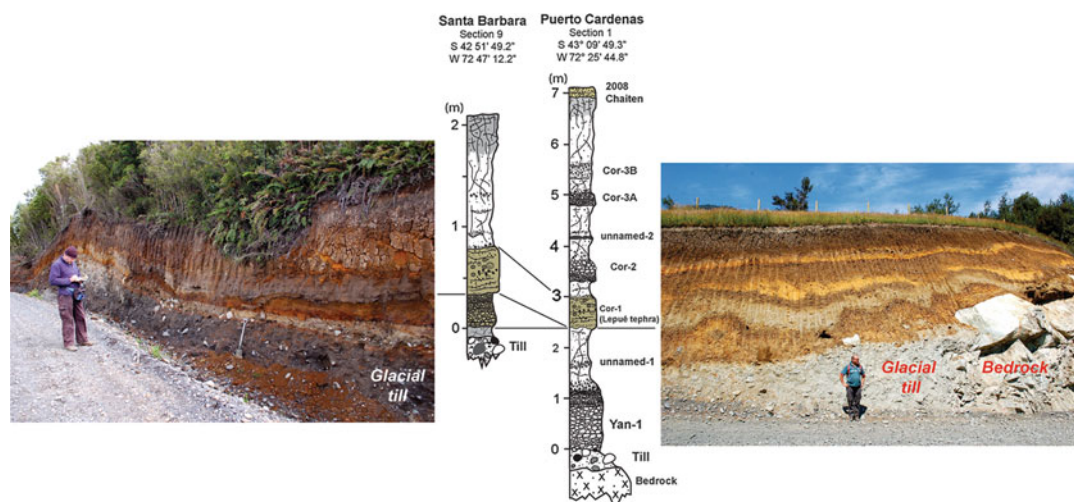


Fig. 3 Stratigraphic columns and corresponding section photos detailing the tephrostratigraphy of deposits at two sites, Santa Barbara and Puerto Cardenas, in the Chaitén sector (42°S) of southern Chile. The tephra notation is from Naranjo and Stern (2004). A key tephra of interest is the prominent decimeter-thick gray tephra layer (Cor-1; now more recently and informally referred to as Lepué tephra) that contains conspicuous accretionary lapilli throughout. This tephra is the product of a large-scale phreatomagmatic eruption sourced from the glaciated Michinmahuida Volcanic Complex (MVC) dated at c. 9,800 ^{14}C year BP. Tephra from the 2008 eruption of Chaitén volcano occurs on the present-day ground surface. Other strongly pedogenically weathered tephra beds represented within these sections have yet to be geochemically characterized and are probably variably sourced from other nearby volcanoes (Puyuhuapi, Melimoyu, Yanteles, and Corcovado). The tephra sequences at both localities rest on glacial till with a minimum age of c. 14,000 ^{14}C year BP (Photos: Brent Alloway)

Tonkin 2010; Dugmore and Newton 2012). Cores taken from lake sediments and peat bogs potentially provide a reliable means to record thin and/or fine-grained distal tephra layers, or at proximal or medial locations where tephra tend to be thicker and may have more restricted dispersal patterns around source vents – for example, in basaltic volcanic fields (Shane and Hoverd 2002). These lake or bog depositional environments allow thin tephra or glass-shard concentrations (cryptotephra) to be preserved amidst organic-bearing sediments (Fig. 6) (de Fontaine et al. 2007; Smith et al. 2013), notwithstanding potential taphonomic difficulties posed by tephra reworking or dispersion (Lowe 2011; Liu et al. 2014). Marine cores, especially from locations downwind of eruption centers, may also contain detailed records of tephra layers or cryptotephra intercalated with sediments (e.g., Guðmundsdóttir et al. 2012; Abbott et al. 2013; Ponomareva et al. 2013b; Austin et al. 2014). Possible reworking of tephra (by currents, ice rafting, bioturbation) adds complexity in some cases (Brendryen et al. 2010; Larsen et al. 2014; Todd et al. 2014).

Together with those from lakes and bogs, many of the records of marine tephra deposits can thus document patterns of explosive volcanism in time and space and integrate the stratigraphic interfingering of eruptives from multiple volcanic sources (Shane et al. 2006; Swindles et al. 2011; Ponomareva et al. 2013a, b). Such compilations are often more comprehensive than those obtainable near volcanic centers because of burial or erosion of eruptives at such proximal locations, but an important caveat is that proximal deposits are typically more compositionally variable than distal deposits (e.g., Smith et al. 2005; Shane et al. 2008a). On this basis, distal deposits usually have a more restricted compositional range than otherwise might be generated during a particular eruptive episode.

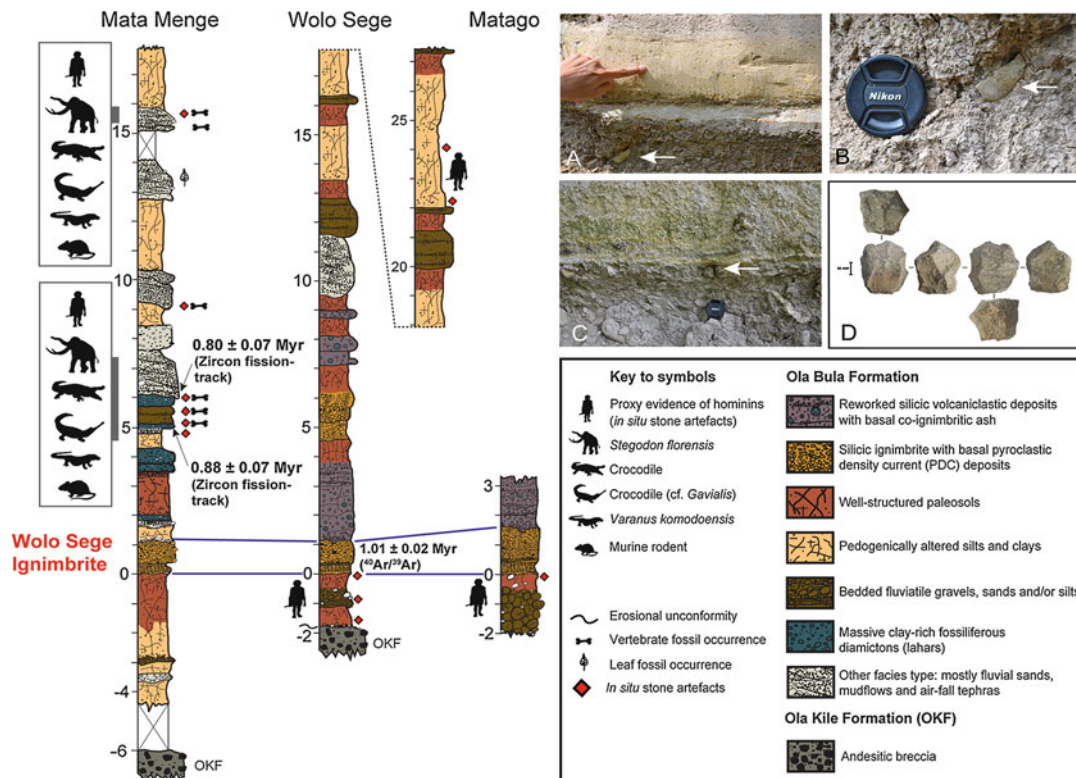


Fig. 4 Stratigraphy associated with hominin stone artifacts and vertebrate fossil remains from the So'a Basin, central Flores, Indonesia (unpublished data of B. V. Alloway, A. Brumm, G. van den Bergh, and R. Setiawan; after O'Sullivan et al. (2001) and Brumm et al. (2010)). The in situ stone artifacts occur immediately beneath a nonwelded (unconsolidated) ignimbrite deposit (Wolo Sege ignimbrite, WSI) that can readily be correlated and distinguished from other enveloping silicic tephra interbeds across the So'a Basin on the basis of its unique depositional architecture as well as its major-element glass-shard composition. The WSI, dated at 1.02 ± 0.02 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ (Brumm et al. 2010), provides important evidence for the presence of hominins on Flores for over 1 million years. (a) The base of WSI at the Wolo Sege section showing distinctive surge-like subunits containing accretionary lapilli and bedding consistent with the density segregation of entrained particles. Note the in situ bifacial flake in the paleosol immediately beneath the base of the WSI (indicated by arrow). (b) Close-up photo of the in situ bifacial flake identified at Wolo Sege. (c) In situ flaked core stone identified at the Matago section on the paleo-ground surface buried by the WSI. (d) Close-up photo showing the detail of the flaked core stone from the Matago section (Photos a–c, Brent Alloway; Photo d, Adam Brumm)

Distal Tephra and Cryptotephra Deposits

Submillimeter-scale studies have involved the development of new approaches to enable cryptotephra, and very thin distal tephra, to be mapped, albeit discontinuously, across landscapes using a range of methods firstly to *detect* and *isolate* glass-shard or crystal concentrations (e.g., Hall and Pilcher 2002; Gehrels et al. 2006; Swindles et al. 2010; Lane et al. 2014) and secondly to *correlate* them with known (previously characterized) deposits using geochemical analyses of glass shards, melt inclusions (glass) within crystals, or crystals (Matsu'ura et al. 2011; Swindles et al. 2013) as described below. Cryptotephra have been discovered in peat, lake, marine, aeolian, or frozen sediments or ice, in deposits in caves or rock shelters, and in soils or paleosols. They (and thin visible tephra) have been detected using ground-penetrating radar, magnetic susceptibility and remanent magnetization, X-radiography, X-ray fluorescence (including use of scanners), spectrophotometry, micro-petrography, enumeration of glass shards, and measurements of total organic carbon and loss on ignition (Turney and Lowe 2001; Gehrels et al. 2008; Lawson et al. 2012). These



Fig. 5 A distal occurrence of fine-grained Mazama tephra, 1–2 cm in thickness and composed mainly of glass shards, shows up as the pale “break” (where the person is touching) in an alluvium-soil sequence on the lowermost terrace alongside the North Saskatchewan River in Edmonton, Alberta, Canada. Multiple buried soils formed on intermittent flood deposits are evident in the section, with the high sedimentation (up-building) rate contributing to the rapid burial and preservation of the thin, fine-grained Mazama tephra as an inconspicuous layer. The Mazama tephra, dated at $7,627 \pm 150$ cal. year BP (Zdanowicz et al. 1999), provides a key isochronous time plane (chronostratigraphic marker bed) for Holocene archaeological and paleoenvironmental studies in the USA and southwestern Canada. Located ~1,450 km northeast of its source (Crater Lake, Oregon), the tephra was first identified here by Westgate et al. (1969) (Photo: Maria Lowe)

novel cryptotephra studies, although not without problems and limitations (e.g., Davies et al. 2007; Payne and Gehrels 2010; Swindles et al. 2011), have documented tephra-fall occurrences at submillimeter scales at distances of hundreds to some thousands of kilometers from source, greatly extending known geographical limits (e.g., Payne et al. 2008; Davies et al. 2010, 2012; Balascio et al. 2011; Cullen et al. 2014). Pyne-O'Donnell et al. (2012) showed that “ultra-distal” cryptotephtras derived from Holocene eruptions in Alaska and the Pacific Northwest occur up to ~7,000 km from source in easternmost North America and one tephra, the Alaskan White River Ash (eastern lobe, erupted around AD 860), occurs over ~7,000 km away in Ireland (Jensen et al. 2014). Lane et al. (2013) identified the c. 75,000-year-old Youngest Toba Tuff tephra as a cryptotephra deposit in Lake Malawi sediments in east Africa, >7,000 km west of the source volcano in Sumatra. Cryptotephra associated with the eruption of the Campanian Ignimbrite in Italy c. 40,000 calendar (cal.) year BP was identified across much of central Europe and the Mediterranean area by Lowe et al. (2012). As noted earlier with regard to visible tephra deposits, cryptotephra studies can help also in elucidating the eruptive history of volcanoes (e.g., Shane et al. 2013).

Ice cores provide detailed and valuable records of volcanism (Davies et al. 2010; Dunbar and Kurbatov 2011; Abbott and Davies 2012; Coulter et al. 2012). Until recently, analytical limitations of geochemical techniques have hindered adequate characterization of ultrafine glass particles (<5 μm) and identification of their eruptive source. Similarly, sulfate records in ice cores may not

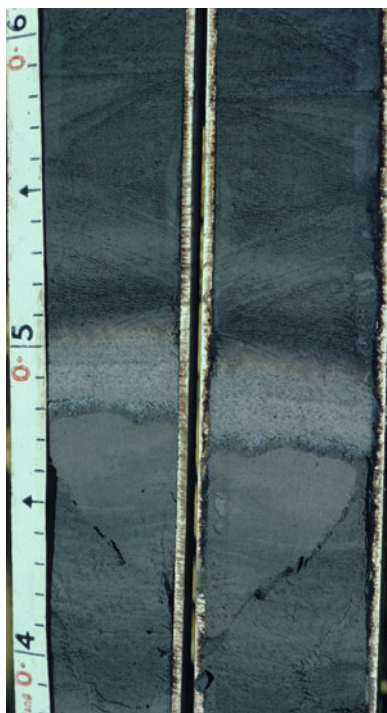


Fig. 6 Close-up of a near-basal part of a lake sediment core from Lake Okoroire, New Zealand, showing (in middle of photo) 3-cm-thick Rerewhakaaitu tephra, erupted $17,496 \pm 462$ cal. year BP from Mt Tarawera in the Okataina Volcanic Centre (Lowe et al. 2013; see Fig. 8 below). Many tiny *black specks* in the pale layer represent free biotite crystals diagnostic of this (and some other) tephras derived from Mt Tarawera. Different sediment colors above and below the tephra reflect a climatically driven change from shrubland/grassland to forest in the region soon after the eruption (Newnham et al. 2003; Alloway et al. 2007). An indistinct uncorrelated tephra lies ~2 cm above the Rerewhakaaitu tephra. Scale marks in centimeters (Photo: David Lowe)

always act as suitable proxies for the occurrence of tephra or cryptotephra deposits composed of (typically sparse) glass shards in the cores (Davies et al. 2010; Abbott and Davies 2012).

Characterizing Tephras and Cryptotephras in the Laboratory

The characterization, or “fingerprinting,” of mineral and glass components of tephras or cryptotephras can be undertaken using a range of analytical methods (Table 1). Such characterization is almost always carried out in conjunction with lithostratigraphic and chronological criteria to obtain cogent correlations (Alloway et al. 2013).

Ferromagnesian Silicate Mineral Assemblages

A common method is to use a petrographic microscope to identify ferromagnesian or mafic mineralogical assemblages where such minerals are abundant, usually at proximal or medial sites. These minerals can be extracted using a magnetic separator together with nontoxic heavy liquids such as sodium polytungstate. With stratigraphic and age constraints, the relative abundances of ferromagnesian minerals may allow a source volcano to be identified. For example, in the Yukon Territory of Canada, Preece et al. (2000, 2011a) showed that tephras erupted from the Aleutian arc-Alaska Peninsula, so-called Type I beds, had low crystal contents comprising mainly pyroxene (and mainly bubble-wall shards), whereas tephras derived from the Wrangell volcanic field and

Table 1 Analytical methods (excluding geochronology) used to characterize glass or minerals in tephra to facilitate their correlation (After Lowe 2011)

Tephra components and properties	Main methods of analysis ^a
Glass shards^b	
Major and minor elements ^c	Electron microprobe
Trace elements ^c including rare earths	LA- or SN-ICP-MS, INAA, SIMS
Sr, Nd, and Pb isotopes	LA-ICP-MS, multi-collector NMS
Shard morphology	Optical microscope, SEM
Melt inclusions (glass)	
Major and minor elements	Electron microprobe
Trace elements	SIMS, LA-ICP-MS
Ferromagnesian silicate minerals	
Assemblages or marker minerals	Petrographic microscope, XRD
Pyroxenes, amphiboles, olivine, or biotite crystals/phenocrysts	Electron microprobe
Crystal geometry	Optical microscope, SEM
Apatite, zircon	
Apatite or zircon ^d crystals/phenocrysts	Electron microprobe, TIMS-TEA
Crystal geometry	Optical microscope, SEM
Fe-Ti oxides	
Major and minor elements	Electron microprobe
Eruption temperatures and oxygen fugacities	Electron microprobe
Feldspars^d	
Plagioclase, anorthoclase, or sanidine crystals/phenocrysts	Electron microprobe

^aLA- or SN-ICP-MS laser ablation or solution nebulization inductively coupled plasma mass spectrometry, INAA instrumental neutron activation analysis, SIMS secondary ionization mass spectrometry (ion probe), NMS nuclide mass spectrometry, SEM scanning electron microscopy, XRD X-ray diffraction, TIMS-TEA thermal ionization mass spectrometry-trace element analysis

^bMay also include glass coats (selvedges) or matrix glass in pumice clasts

^cMajor elements expressed as oxides usually are defined as >1 wt%, minor element oxides as 0.1–1 wt%, and trace elements as <0.1 wt% or <1,000 parts per million (ppm) of the element (not oxides)

^dAnalyses of these minerals generally are less useful for correlating individual tephra

Hayes volcano, Type II beds, generally had high crystal contents comprising mainly hornblende (and mostly pumiceous shards). In New Zealand, orthopyroxene (mainly hypersthene) is dominant in tephra erupted from the Taupo Volcanic Centre since c. 30,000 cal. year BP, whereas biotite, hornblende, cummingtonite, or orthopyroxene predominate in tephra erupted from the Okataina Volcanic Centre over the same period (Lowe et al. 2008).

In some cases an individual tephra can be identified using distinctive, diagnostic marker minerals, such as aegirine and aenigmatite in the Tuhua Tephra that were erupted from peralkaline Mayor Island volcano c. 7,000 cal. year BP in New Zealand. However, the absence of diagnostic minerals does not necessarily negate correlation because minerals such as olivine, biotite, and hypersthene can be dissolved comparatively quickly in some very acid peat bogs (within 700 years; Hodder et al. 1991) or in soil-forming environments (Lowe 1986; Churchman and Lowe 2012). Ferromagnesian minerals and Fe-Ti oxides also tend to be sparse or absent at distal localities, dropping out from proximal or medial ash clouds earlier because of their high density (Juvigné and Porter 1985).

Although of limited application, the crystal geometry (crystal width) of apatite (a phosphate-group mineral) was shown to be useful, along with apatite trace-element data, for differentiating beds in a study of Late Ordovician K-bentonites in the USA by Sell and Samson (2011). Similarly,

Donoghue et al. (1991) showed that two distinct crystal geometries of olivine (skeletal, non-skeletal) were useful in correlating some andesitic tephra in New Zealand.

Major-Element Analysis of Glass Shards, Melt Inclusions, and Minerals

The electron microprobe enables a range of tephra components to be analyzed for major elements on a grain-by-grain basis: individual glass shards, glassy coatings on crystals, melt inclusions (glass preserved within crystals including quartz, pyroxenes, amphiboles), pumice fragments, and loose crystals or phenocrysts including various ferromagnesian silicate minerals, apatite, zircon, and Fe-Ti oxides such as titanomagnetite (Table 1). The main advantage of the microprobe and other single-grain techniques is that they allow mixed or heterogeneous populations to be identified. Because volcanic glass is amorphous, its analysis by microprobe needs especially careful sample preparation and mounting, the use of appropriate standards, and optimum probe-operating conditions to derive accurate and robust data (Kuehn et al. 2011; Hall and Hayward 2014; Pearce et al. 2014; Suzuki et al. 2014).

Usually a defocused (e.g., 10–20 μm) or rastered beam is deployed to minimize the mobilization of Na, although protocols that use narrower beam diameters (3–5 μm) without loss of Na have been recently developed for analyzing fine-grained glass shards, as occur in distal or ultra-distal tephra or cryptotephra or glasses with microlites (Hayward 2012; Pyne-O'Donnell et al. 2012; Hall and Hayward 2014). Glass microprobe analyses are usually normalized (summed to 100 %, most, but not all, of the deficit being attributable to water) to enable useful comparisons of analyses (Shane 2000; Lowe 2011; Westgate et al. 2013a). Using stratigraphic or age constraints, and usually also a knowledge of geochemical affinities of potential source rocks/deposits and spatial distribution patterns, the microprobe analysis of glass may allow tephra source volcanoes to be identified, and individual eruptives may also be correlated in some cases where compositions through time have changed from one eruptive event to the next. Complexities arise where glass analyses show heterogeneity, a consequence potentially of (i) mingling or mixing of separate batches of magmas that were tapped simultaneously or sequentially as eruptions proceeded (e.g., Tryon et al. 2010; Turner et al. 2011b), (ii) major-element evolution by fractional crystallization or crustal assimilation (Bogaard and Schminke 1985; Ukstins Peate et al. 2008; Óladóttir et al. 2012), (iii) blending of thin tephra in soil-forming or cryogenic environments (Lowe 1986; Eden et al. 2001; Dugmore and Newton 2012), or (iv) post-depositional dissemination of glass shards in peat, lake, or marine sediments (Gehrels et al. 2006; Allan et al. 2008; Abbott et al. 2013). Heterogeneity arising from magmatic or volcanic eruption processes accompanied by changes in wind direction warns of the difficulty of characterizing (thus fingerprinting) tephra beds using a limited set of distal samples from restricted dispersal sectors (Shane et al. 2008a). Another problem can arise with analyses of melt inclusions where these do not reflect the full compositional range of glass shards or matrix glass (e.g., Shane et al. 2008b; Chesner and Luhr 2010; Allan et al. 2013) or they show a pattern different from that associated with matrix glass analyses (e.g., Kilgour et al. 2013). Once recognized, such compositional variability can enhance correlation by providing additional fingerprinting criteria, but sampling from the full spatial and temporal range of deposits of an eruptive sequence is required (Alloway et al. 2013).

The correlation of andesitic or basaltic tephra using glass chemistry generally can be complicated for various reasons including the multiplicity of units, the paucity of suitable glass for microprobing (shards may contain micro-inclusions and can be highly vesicular), susceptibility of glass to weathering, and wide compositional ranges and potential heterogeneity as noted previously (Moebis et al. 2011; Shane and Zawalna-Geer 2011; Óladóttir et al. 2012). Platz et al. (2007) provided a procedure to evaluate glass compositional variability arising from the inadvertent

microanalysis of plagioclase microlites in shards using a wide beam, but the recent use of narrower beam diameters is helping to obviate this problem (Hayward 2012; Pearce et al. 2014).

Analyses by microprobe of ferromagnesian silicate minerals, such as biotite (Shane et al. 2003; Smith et al. 2011) and cummingtonite (Matsu'ura et al. 2012), apatite (a phosphate-group mineral) (Sell and Samson 2011), and Fe-Ti oxides such as titanomagnetite and ilmenite (Shane 1998; Preece et al. 2011b; Marcaida et al. 2014), have also been used for tephra fingerprinting. In some cases, and after taking into account compositional zoning within crystals, trace elements such as Mg, Cl, Mn, Fe, Ce, and Y identified in apatite crystals and phenocrysts provide a means of distinguishing or matching tephras (Sell and Samson 2011). The eruption temperature and oxygen fugacity (oxidation state of magma) of rhyolitic tephras – estimated using single-grain EMPA of Fe-Ti oxide pairs of titanomagnetite and ilmenite – provide another way to correlate tephras and, in some cases, magma batches within an eruptive sequence (Smith et al. 2005; Preece et al. 2011b; Marcaida et al. 2014).

Trace-Element and Isotope Analysis of Glass

Although the microprobe is now the key analytical tool for undertaking major-element analyses of glass, tephras or cryptotephras cannot always be distinguishable uniquely by major-element data alone. In these cases, other analytical methods are needed (Westgate et al. 2013c). Trace-element analyses of glass separates from tephra or cryptotephra deposits offer a greater range of elements for use in correlation/provenance studies and may also provide additional information on volcanic petrogenesis. In the last decade, trace-element techniques have become more common, the most widely available being laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (e.g., Albert et al. 2012; Ponomareva et al. 2013a; Sulpizio et al. 2013) (Table 1). Pearce (2014) provides protocols for the application of LA-ICP-MS to glass shards. Around 150 individual glass shards can be analyzed for about 30 trace elements in 1 day using LA-ICP-MS (Pearce et al. 2011). Comprehensive studies using this method were undertaken on Pleistocene tephras in northern New Zealand (Pearce et al. 2008b) and in marine cores from Ocean Drilling Project (ODP) Site 1123 (Allan et al. 2008). The most useful elements for correlating and distinguishing between the ODP Site 1123 tephras were found to be the abundances of Rb, Ba, Sr, Y, Zr, Hf, Mg, Mn, and Ti and trace-element ratios including Rb/Sr, Ba/Sr, Zr/Y, Y/Th, Ba/Th, and Rb/Sm. Using trace-element data for glass shards, Allan et al. (2008) demonstrated that (i) tephras with similar major-element compositions (e.g., Kawakawa tephra vs. Omataroa tephra) were easily distinguishable (Fig. 7) and (ii) two previously unidentified repeated sections of ODP cores 1123A (~4.5 m thick) and 1123C (~7.9 m thick) were recognized (Allan et al. 2008). As with the microprobe, there is a possibility of microlites affecting trace-element characterizations of individual shards via LA-ICP-MS, and so anomalous assays need to be evaluated carefully (Abbott et al. 2013).

Analyses of isotopes of Sr, Nd, and Pb in glass (or pumices) have been utilized in several studies to help determine tephra source volcanoes (e.g., Roulleau et al. 2009; Westgate et al. 2008, 2011; Giaccio et al. 2013).

Comparing Compositional Data Using Graphical, Numerical, and Statistical Methods

Major- or trace-element datasets obtained from analyses of glass or minerals may be displayed and compared, and hence compositional variability evaluated, using various methods: graphical (e.g., bivariate or trivariate plots), numerical (e.g., similarity coefficients), or statistical (e.g., statistical distance measure, dendrograms, discriminant function analysis, principal components analysis) (Pearce et al. 2008a; Bourne et al. 2010; Lowe 2011; Sell and Samson 2011). In many cases, the bivariate plots alone can provide sufficient guidance to enable anomalous data points to be identified

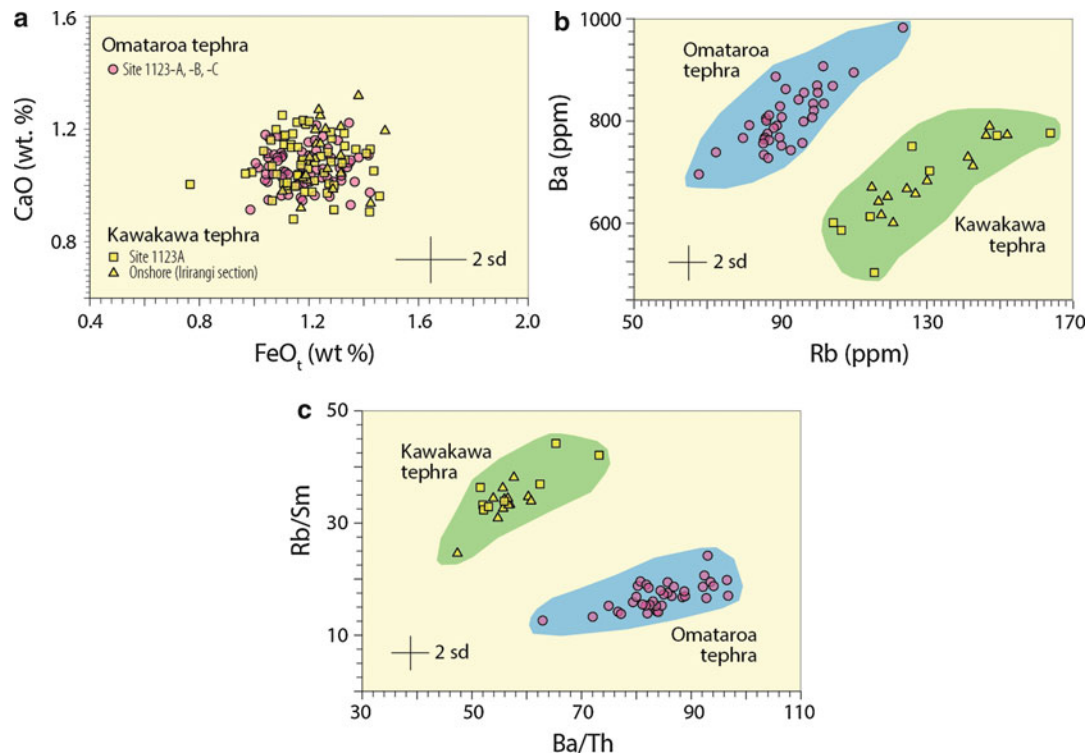


Fig. 7 Bivariate plots for some major and trace elements derived from analyses of individual glass shards from two New Zealand tephra, Omataroa (c. 31,600 cal. year BP, erupted from Okataina Volcanic Centre) and Kawakawa (c. 25,400 cal. year BP, erupted from Taupo Volcanic Centre), identified in marine cores (a), (b), and (c) from ODP Site 1123 about 1,200 km east of New Zealand (Modified after Allan et al. 2008, p. 2351, with permission of Elsevier). (a) CaO versus FeO_t (total iron expressed as FeO) derived by electron microprobe. Glass analyses from an onshore occurrence of Kawakawa tephra (at Irirangi) are also shown for comparison. The plot shows that the analyses of marine and onshore samples of Kawakawa tephra are identical and that Kawakawa and Omataroa tephra cannot be distinguished using these two oxides alone. In contrast, trace-element concentrations (in ppm), derived by LA-ICP-MS, in (b) and (c), show that the tephra are distinctly different with respect to their elements/element ratios and hence can be readily distinguished

(and possibly explained using compositional databases for comparison) and potential correlations or otherwise established with reasonable likelihood, especially where multiple criteria provide independent support, such as concordance of glass major- and trace-element data together with Fe-Ti oxide data (e.g., see Preece et al. 1999, 2011b). In other situations, however, statistical methods such as principal components analysis can allow units to be distinguished objectively on the basis of multiple oxides or elements (not just two or three) analyzed from glass shards or crystals (e.g., Tryon et al. 2010; Chiasera and Cortés 2011; Sell and Samson 2011).

Dating Tephra (Tephrochronometry)

Tephra may be dated directly using primary minerals (e.g., zircon, hornblende, K-feldspars, biotite, quartz) or glass from within the tephra layer, or indirectly on either enclosing or encapsulated material, using a range of methods including radiometric, incremental (e.g., varves, layering in ice), and age equivalence (Table 2) (Svensson et al. 2008; Alloway et al. 2013; Zalasiewicz et al. 2013). These ages can then be transferred from one site to another where the tephra is recognized using the

Table 2 Methods used for dating tephtras directly or indirectly (after Lowe 2011)

Main method	Applications
Radiometric	Radiocarbon dating (radiometric/beta counting, AMS) ^a Fission-track dating of zircon or glass-ITPFT or glass-DCFT dating Argon isotopes (K/Ar, Ar/Ar including SCLP/F, LIH) Luminescence dating (TL, OSL, IRSL, pIR-IRSL) U-series including (U-Th)/He, U-Pb, and ²³⁸ U/ ²³⁰ Th zircon dating (SIMS/TIMS, SHRIMP, LA-ICP-MS) Electron spin resonance ²¹⁰ Pb, ¹³⁷ Cs, ³ He, and ²¹ Ne surface exposure dating
Incremental	Dendrochronology, varve chronology, layering in ice cores (ice sheets/caps, glaciers)
Age equivalence	Magnetopolarity, paleomagnetic secular variation, astronomical (orbital) tuning, correlation with marine oxygen isotope stages, climatostratigraphy, biostratigraphy, palynostratigraphy, paleopedology
Age modeling	Various age-depth methods including Bayesian flexible depositional modeling and wiggle matching, spline-fit modeling
Relative	Obsidian hydration dating, amino acid racemization
Historical	Eyewitness accounts or observations (e.g., via remote sensing)

^aAMS accelerator mass spectrometry, *ITPFT* isothermal-plateau fission track, *DCFT* diameter-corrected fission track, *SCLP/F* single-crystal laser probe or fusion, *LIH* laser incremental heating, *TL* thermoluminescence, *OSL* optically stimulated luminescence, *IRSL* infrared stimulated luminescence, *pIR-IRSL* post infrared-infrared-stimulated luminescence, *SIMS* secondary ionization mass spectrometry, *TIMS* thermal ionization mass spectrometry, *SHRIMP* sensitive high-resolution ion microprobe, *LA-ICP-MS* laser ablation inductively coupled plasma mass spectrometry

lithostratigraphic and compositional-based methods described above. Only the main radiometric methods, and age modeling, are touched on here.

For tephtras erupted within the past c. 60,000 calendar years, the radiocarbon (¹⁴C) technique (e.g., Hogg et al. 2007) remains the most important method for developing calibrated age models. In recent years, the advantages of using pollen concentrates and terrestrial plant macrofossils (e.g., leaves, twigs), rather than bulk organic samples, as reliable dating materials via AMS have been demonstrated (Newnham et al. 2007; Staff et al. 2011). Together with dendrochronological wiggle-matching methods (Hogg et al. 2012; Yin et al. 2012), Bayesian flexible depositional age modeling has added a revolutionary aspect to the construction of enhanced and more precise chronologies in tephrochronology involving ¹⁴C and other dating methods (Blockley et al. 2008; Smith et al. 2013). Lowe et al. (2013) dated late Quaternary tephtras in New Zealand by modeling ¹⁴C age data using two Bayesian-based programs, Bacon (Blaauw and Christen 2011) and OxCal's *P_Sequence* function (Bronk Ramsey 2009) and the IntCal09 dataset (Fig. 8). Lohne et al. (2013) also used *P_Sequence* and IntCal09 to obtain high-precision ages of 12,066 ± 42 and 10,210 ± 35 cal. year BP (±1σ) for the Vedde and Saksunarvatn tephtras, respectively, from sediments in Kråkenes Lake, Norway. Similarly, the AT tephtra of Japan was dated to 30,009 ± 189 cal. year BP (95 % probability) using *P_Sequence* modeling of ¹⁴C data and varves (Smith et al. 2013). Vandergoes et al. (2013) used OxCal's *Tau_Boundary* function, also Bayesian, to precisely date the Kawakawa/Oruanui tephtra of New Zealand to 25,358 ± 162 cal. year BP (95 % probability).

Another key advance in tephrochronology has been the development of the isothermal-plateau fission-track dating method (ITPFT) for glass (Westgate 1989; Alloway et al. 2004b, 2013; Westgate et al. 2013b). ITPFT and the diameter-corrected fission-track method (Sandhu and Westgate 1995) have enabled ages to be obtained on many distal vitric-rich tephtras that previously were unable to be dated because of low abundance of dateable mineral constituents, fine grain size, and the presence of detrital grains. Examples of such applications include dating Quaternary glacioeustatic sedimentary

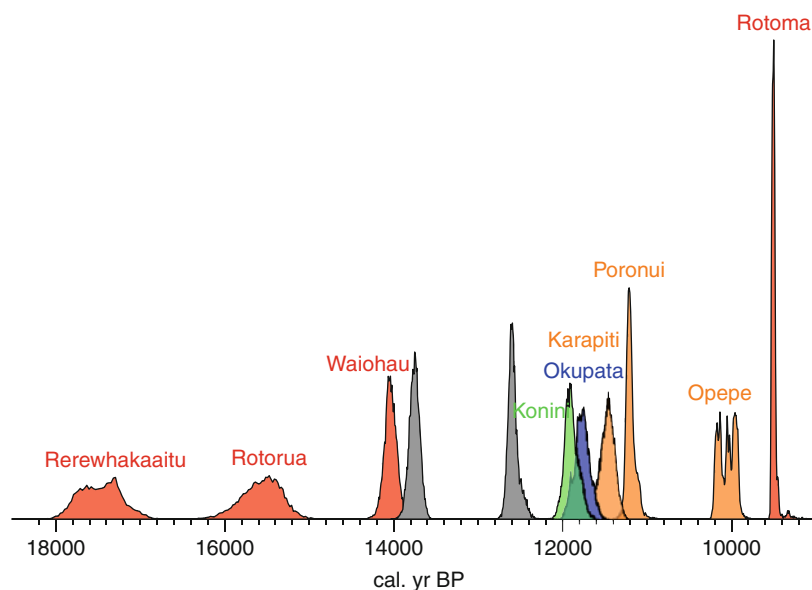


Fig. 8 Bayesian-derived age models (95 % probability) for nine late Quaternary tephras in New Zealand (From Lowe et al. 2013, p. 179, with permission of Elsevier). Probability plots are colored according to tephra source volcanoes: *red*, Okataina; *orange*, Taupo; *green*, Taranaki; and *blue*, Tongariro. Gray plots show the start and end ages of the late glacial cool episode, designated climate event NZce-3 by Barrell et al. (2013), in part constrained chronologically by the ages on the adjacent tephras

cycles in the Wanganui Basin (Alloway et al. 1993; Pillans et al. 2005) and dating initial loess deposition in Alaska at ~3 million years ago (Westgate et al. 1990). The glass-FT techniques have been used, for example, also to test chronologies based on alternative methods (such as magnetic polarity and astronomical tuning) for marine tephra sequences (Alloway et al. 2005; Allan et al. 2008) and for fossiliferous alluvial and lacustrine sediments in Beringia (Preece et al. 2011b; Westgate et al. 2013a).

Where suitable minerals are available (e.g., sanidine, biotite, leucite, anorthoclase), the $^{40}\text{Ar}/^{39}\text{Ar}$ method has been useful, such as dating the Laacher See tephra in Germany (Bogaard 1995); the ultra-distal to distal deposits of the Youngest Toba Tuff tephra of Indonesia (Westgate et al. 1998; Storey et al. 2012); a widespread Holocene tephra erupted from Ulleungdo stratovolcano in South Korea (Smith et al. 2013); a 400,000-year-old sequence of eruptives from Nemrut volcano preserved in Lake Van, eastern Anatolia in Turkey (Sumita and Schminke 2013); and the distal tephras preserved in lacustrine and fluvial sediments of intermontane basins of central Italy (Giaccio et al. 2013). A relatively new method for dating proximal pyroclastic deposits, previously applied to petrologic studies, is the use of U-Pb analyses to date zircons (Schmitt 2006; Dickinson et al. 2010; Wilson et al. 2010). Luminescence and (U-Th)/He dating methods are also being applied systematically to tephra deposits (Danišik et al. 2012; Biswas et al. 2013).

A trend in dating lake sediment sequences containing tephras or cryptotephra is to apply multiple methods, as exemplified by Staff et al. (2013) and Sirocko et al. (2013).

Conclusions

Tephrochronology is the use of primary tephra or cryptotephra as isochrons to link and synchronize geological, paleoenvironmental, or archaeological sequences or events, or soils, and, uniquely,

to transfer relative or numerical ages to them using stratigraphic information and mineralogical and geochemical compositional data, especially from individual glass-shard analyses, obtained for the tephra/cryptotephra. To function therefore as an age-equivalent correlation and chronostratigraphic dating tool, tephrochronology can be undertaken in three steps: (i) mapping and describing tephra and determining their stratigraphic relationships, (ii) characterizing tephra or cryptotephra in the laboratory, and (iii) dating them using a wide range of geochronological methods. Tephrochronology is also an important tool in volcanology, informing studies on volcanic petrology, volcano eruption histories and hazards, and volcano-climate forcing. Although limitations and challenges remain, multidisciplinary applications of tephrochronology continue to grow markedly (e.g., Alloway et al. 2013; Lane et al. 2014).

Acknowledgments

We thank editors Jeroen Thompson and Jack Rink for inviting us to write this entry and for their suggestions, reviewer Vera Ponomareva for her helpful comments, Megan Balks and Adam Brumm for providing photographs, and Chris Hayward and John Westgate for furnishing preprints. Elsevier kindly allowed us to use previously published material (Figs. 7 and 8). The entry was funded in part by the New Zealand Marsden Fund (project 10-UOW-056 to DJL entitled “New views from old soils”), administered by the Royal Society of New Zealand, and it is an output also of the INTREPID Tephra-II project (INQUA project 1307s) “Enhancing tephrochronology as a global research tool through improved fingerprinting and correlation techniques and uncertainty modeling (phase II),” an initiative of the International Focus Group on Tephrochronology and Volcanism (INTAV) supported by the Stratigraphy and Chronology Commission of the International Union for Quaternary Research (INQUA).

Cross-References

- ▶ [14C Dating](#)
- ▶ [210Pb Dating](#)
- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Biostratigraphy](#)
- ▶ [Dendrochronology, Volcanic Eruptions](#)
- ▶ [Fission Track Dating](#)
- ▶ [Geochronology](#)
- ▶ [Ice Cores](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Lacustrine Environments \(14C\)](#)
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- ▶ [U-Th: He Dating](#)
- ▶ [Varve Chronology](#)
- ▶ [Volcanic Glass \(Fission Track\)](#)
- ▶ [Zircon](#)

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Kimberlites (K-Ar/Ar-Ar)

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Synonyms

⁴⁰Ar/³⁹Ar geochronology; Conventional K–Ar dating; K–Ar dating; Kimberlite clan rocks

Definitions

Potassium-argon (K–Ar) dating: Scientific dating method based on the natural decay of ⁴⁰K to ⁴⁰Ar, where the ratio of the parent isotope, ⁴⁰K, relative to the daughter product ⁴⁰Ar (radiogenic ⁴⁰Ar or ⁴⁰Ar*) is used to calculate the age of a sample.

⁴⁰Ar/³⁹Ar (Argon-Argon) geochronology: A variation of the K–Ar method, where the ⁴⁰K content is determined indirectly by neutron activation of ³⁹K to ³⁹Ar; here, the ⁴⁰Ar* to ³⁹Ar ratio is proportional to age, with sample ages calculated relative to co-irradiated standards of known age.

Excess argon: ⁴⁰Ar, aside from atmospheric ⁴⁰Ar, that is incorporated into rocks and minerals by processes other than in situ radioactive decay of ⁴⁰K. Excess argon results in ⁴⁰Ar to ³⁶Ar > 295.5 and may be identified from isochron plots.

Inherited argon: Radiogenic argon (⁴⁰Ar*) included in rocks and minerals through contamination by older material or retention of ⁴⁰Ar* from a previous event, e.g., feldspar xenocrysts in extrusive volcanic rocks that are not isotopically reset by the magmatism and retain some proportion of the ⁴⁰Ar* generated between the times of xenocryst crystallization and magma eruption.

Extraneous argon: A *sac* term for excess or inherited argon.

Kimberlites (Definitions modified from Mitchell (1986)): Small volume, volatile-rich, potassic ultramafic igneous rocks that usually occur as diatremes, but also as dykes and sills and sometimes contain diamonds. Kimberlites typically have an inequigranular texture due to abundant crustal and mantle fragments set in a fine-grained matrix. Two varieties are recognized:

- i. *Group I kimberlites*: CO₂-rich, potassic ultramafic igneous rocks with an inequigranular texture. Megacryst/macrocryst minerals include olivine, ilmenite, pyrope garnet, phlogopite, enstatite, and chromite. Matrix minerals include olivine, phlogopite, perovskite, spinel, diopside, monticellite, apatite, calcite, and serpentine.
- ii. *Orangeites (or Group II kimberlites)*: H₂O-rich, ultrapotassic, peralkaline igneous rocks, often with an inequigranular texture. Megacryst/macrocryst minerals include phlogopite,

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olivine, pyrope garnet, enstatite, and chromite. Matrix minerals typically include abundant phlogopite and lesser clinopyroxene, spinel, perovskite, apatite, REE-phosphates, K-Ba-titanates, rutile, and ilmenite. More evolved orangeites may contain matrix sanidine, K-richterite, and Zr-silicates.

Lamproites (Definition modified from Mitchell (1995)): Small volume, peralkaline, ultrapotassic igneous rocks that occur as diatremes, cinder cones, dykes, and sills. Megacryst/macrocryst minerals include olivine, pyrope garnet, phlogopite, enstatite, and chromite. Minerals typical of lamproites include leucite, titanian phlogopite phenocrysts, titanian tetraferriphlogopite, Ti-K-richterite, diopside, sanidine, K-Ba-titanates (e.g., priderite), and K-Zr-silicates (e.g., wadeite).

Introduction

Kimberlites and related rocks are volumetrically insignificant igneous rocks but have received considerable scientific attention because they are a primary host rock for diamonds and contain a large range of xenoliths (rock fragments) from the underlying crust and mantle. Kimberlites and related rocks have proven difficult to date accurately, due to their propensity to alteration and the almost ubiquitous presence of crustal and mantle xenolithic material. Over the years, several scientific dating methods have been applied to kimberlite geochronology, including the K-Ar, $^{40}\text{Ar}/^{39}\text{Ar}$, U-Pb, Rb-Sr, and fission track methods. Currently, the most widely applied techniques involve Rb-Sr dating of phlogopite and U-Pb dating of perovskite methods (see reviews by Allsopp et al. 1989 and Heaman et al. 2003). The K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ techniques (for information on these methods, see McDougall and Harrison 1999) are less commonly employed, due to the common presence of extraneous argon (excess or inherited argon) in kimberlitic minerals (e.g., phlogopite), which results in anomalously old ages. Nonetheless, the $^{40}\text{Ar}/^{39}\text{Ar}$ dating method can provide useful kimberlite and related rock age information, provided that samples are carefully chosen and appropriate experimental procedures are employed to test for extraneous argon (Phillips et al. 1998, 1999; Phillips et al. 2012a).

Historical Development

The earliest attempts to date kimberlitic rocks using the K-Ar dating method focused on kimberlites located in Kentucky and Kansas. These studies targeted large phlogopite grains (megacrysts), which yielded variable age results that were difficult to interpret (Zartman et al. 1967; Brookins 1969; Brookins and Naeser 1971). Many subsequent attempts to date kimberlites using conventional K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating methods also utilized large phlogopite macrocrysts or phlogopite-bearing mantle xenoliths (e.g., Macintyre and Dawson 1976; Kaneoka and Aoki 1978). Although reliable K-Ar ages consistent with stratigraphic or other isotopic evidence were reported for some kimberlitic phlogopite samples, most coarse phlogopite grains produced anomalously old K-Ar or $^{40}\text{Ar}/^{39}\text{Ar}$ ages as well as disturbed ^{40}Ar – ^{39}Ar step-heating spectra (see reviews by Phillips et al. 1999; Phillips 2012).

The anomalously old ages are consistent with crystallization of phlogopite macrocrysts/megacrysts prior to kimberlite eruption, and are usually attributed to the presence of inherited argon, although some authors also invoked the presence of excess argon to explain some results

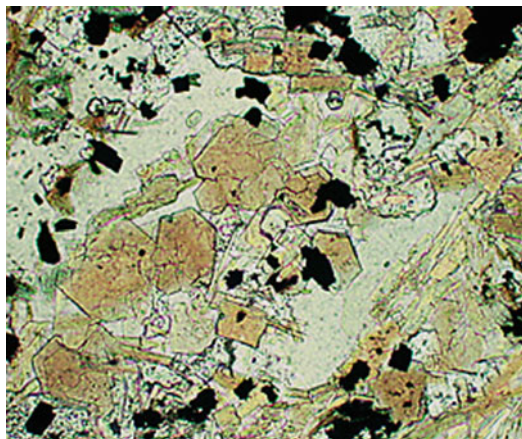


Fig. 1 Photomicrograph showing euhedral, matrix phlogopite grains in a magmatic kimberlite. Note the presence of other matrix mineral (e.g., spinel) inclusions in the phlogopite grains, confirming a magmatic paragenesis. The field of view of the photomicrograph is 2 mm

(see reviews by Phillips 1991, 2012; Hopp et al. 2008). Allsopp and Roddick (1984) conducted the first systematic study to compare $^{40}\text{Ar}/^{39}\text{Ar}$ results from large phlogopite macrocrysts and groundmass phlogopite grains extracted from the Dokolwayo orangeite in Swaziland. This study obtained older apparent $^{40}\text{Ar}/^{39}\text{Ar}$ ages from large phlogopite macrocrysts, but concordant (plateau) age results for groundmass phlogopite crystallized from the orangeite magma. Consequently, more recent studies have focused on matrix phlogopite grains, which, if unaltered, can provide reliable age results for kimberlite magmatism (see Phillips et al. 1998, 1999; O'Brien et al. 2007; Phillips et al. 2012a).

Key Concepts

Sample Selection and Characterization

Phlogopite mica is the preferred mineral for K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of kimberlites and related rocks, due to its common occurrence and relatively high K content (~8 wt%). Phlogopite occurs in these rocks as primary and secondary grains in entrained mantle xenoliths, as megacrysts and macrocrysts (crystal fragments) and as groundmass crystallites of the kimberlite and related rock melts (Mitchell 1986, 1995). Orangeites and lamproites also contain other potassium-bearing minerals that may be suitable for K-Ar or $^{40}\text{Ar}/^{39}\text{Ar}$ dating, such as sanidine, K-richterite, K-Ba-titanates, and K-Zr-silicates (Jaques et al 1984; Phillips et al. 2012a); however, few studies have been conducted on these phases.

Careful sample selection and characterization is key to obtaining reliable $^{40}\text{Ar}/^{39}\text{Ar}$ ages for kimberlites and related rocks because of the presence of extraneous argon in phlogopite xenocrysts and phenocrysts. Therefore, petrographic characterization of kimberlite and related samples is a minimum requirement for identifying samples hosting suitable matrix phlogopite (or other K-bearing magmatic minerals). The best material for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology is fresh groundmass phlogopite that is sufficiently coarse grained ($>100\text{ }\mu\text{m}$) to allow routine mineral separation; these grains are usually restricted to magmatic kimberlite and related rock occurrences (e.g., dykes and sills). Volcaniclastic samples are generally unsuitable, due to fine grain sizes, heterogeneous mineral populations, and susceptibility to alteration.

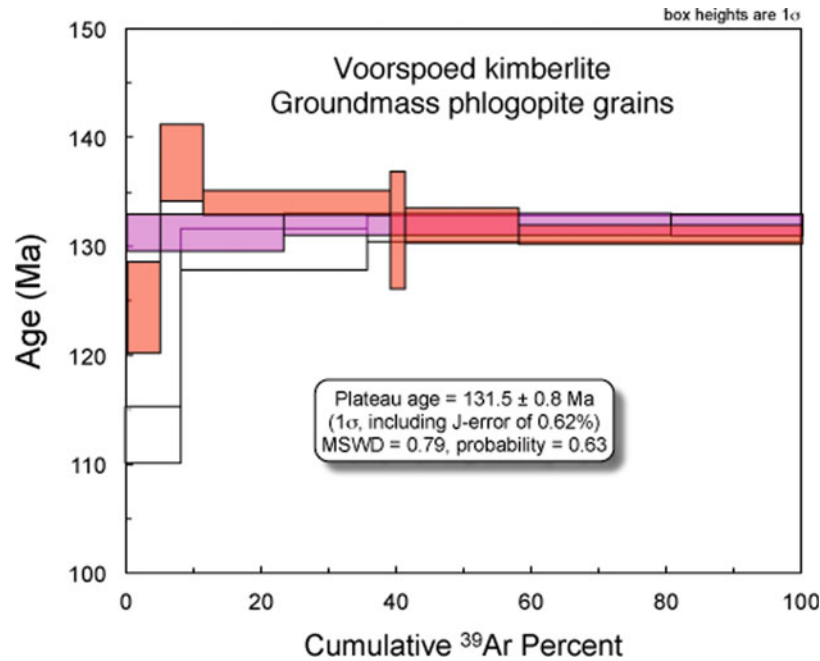


Fig. 2 $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating age spectra obtained on individual matrix tetraferriphlogopite grains from the Voorspoed kimberlite, South Africa (Modified from Phillips et al. 1998). Aside from a few discordant low temperature results, most steps show concordant results, averaging 131.5 ± 1.6 Ma (2σ). Note: each *color* represents a separate step-heating experiment on a single phlogopite grain; the *boxes* represent individual step-heating analyses, with the width indicating the relative proportion of ^{39}Ar released and bar heights indicating plus/minus one sigma uncertainties

Where present, magmatic (i.e., matrix) micas in Group I kimberlites belong to the kinoshitalite compositional series. Orangeites and lamproites typically contain abundant, euhedral tetraferriphlogopite groundmass crystals (Fig. 1). In thin section, matrix phlogopite grains may be distinguished from xenocrysts/phenocrysts by their finer grain size and the common presence of inclusions of other groundmass minerals such as spinel (see Fig. 1). In cases where matrix phlogopite is uncommon (e.g., many Group I kimberlites), more effort is usually required to locate rare matrix minerals or phlogopite associated with reaction rims on garnets or other xenocrysts (Phillips et al. 2012b). Once phlogopite mineral separates are obtained, it is desirable to analyze a number of single phlogopite grains using the $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating method to assess age reliability (see below).

$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology of Kimberlites and Related Rocks

As noted, the attainment of reliable $^{40}\text{Ar}/^{39}\text{Ar}$ age data for kimberlites and related rocks is dependent on the selection of suitable, unaltered, magmatic minerals such as matrix phlogopite. Despite the fine grain size of matrix phlogopite grains ($<200\ \mu\text{m}$), the advent of microanalytical $^{40}\text{Ar}/^{39}\text{Ar}$ laser-probe dating techniques (e.g., Phillips et al. 1998, 1999) permits step-heating analyses of single groundmass phlogopite grains (or aliquots of a few grains). This approach avoids problems associated with bulk mineral separates, such as contamination by phlogopite xenocrysts and phenocrysts hosting extraneous argon, and also allows assessment of other potential problems such as thermal- or alteration-induced argon loss and recoil effects (see Hall (2013) for a discussion of recoil effects). An example of an $^{40}\text{Ar}/^{39}\text{Ar}$ experiment conducted on single matrix tetraferriphlogopite grains ($\sim 200\ \mu\text{m}$ in size) from the Voorspoed orangeite (South Africa) is shown in Fig. 2 (see Phillips et al. 1998 for details). In this case, three phlogopite grains were

individually step-heated in 3–6 increments. Aside from minor discordance associated with the lowest temperature steps, all three grains show reproducible results, with a weighted mean age 131.5 ± 1.6 Ma (2σ). This and other examples (see Phillips et al. 1999) demonstrate the high precision capability of the $^{40}\text{Ar}/^{39}\text{Ar}$ laser-probe method, provided that suitable sample material is available.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Fission Track Dating](#)
- ▶ [Geochronology](#)
- ▶ [Igneous Rocks \(K-Ar\)](#)
- ▶ [Igneous Rocks \(Rb-Sr geochronology\)](#)
- ▶ [Mantle Rocks \(K-Ar/Ar-Ar\)](#)
- ▶ [Minerals \(Ar-Ar\)](#)
- ▶ [Rb-Sr Dating](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Uranium-Lead, Igneous Rocks](#)
- ▶ [Uranium-Lead, Rubidium-Strontium, Kimberlite](#)
- ▶ [Uranium-Lead, Zircon](#)
- ▶ [Volcanic Rocks \(K-Ar/Ar-Ar\)](#)
- ▶ [Zircon](#)

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Sediment Mixing Rate, ^{210}Pb and ^{234}Th

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Definition

Sediment mixing – the movement or redistribution of deposited sediments within a sediment column by physical and/or biological means such that the sediment is moved from its original sequence or position of deposition.

Introduction

Two members of the naturally occurring uranium and thorium decay series, ^{210}Pb (half-life 22.3 years) and ^{234}Th (half-life 24.1 days), may occur in excess of their parent activity at depth within the sediment column of aquatic systems either from sediment accumulation or downward mixing of sediment particles. The downward mixing of sediment particles is produced by physical processes such as current or wave action and biological processes such as burrowing organisms. Being aware of and understanding sediment mixing is important for several reasons. The most basic of these reasons relates to using sediments to interpret the past. Sediments are deposited in sequential order and thus provide a temporal record of surface processes and a historical record of material input. This information can have a variety of uses from understanding past climate or environmental changes to reconstruction of the pollution or contaminant history of a drainage basin. Interpreting the sequential sediment record or layers is sometimes described by the analogy of reading the layers like they are pages in a book. Now imagine the pages in the book have been rearranged. This rearrangement alters or smears the sediment record which can influence the preservation of physical sedimentary structures (Nittrouer and Sternberg 1981). How much the sediment record is altered depends on the intensity, depth, and nature of the sediment mixing in relation to the sediment accumulation rate (Smoak and Patchineelam 1999). Sediment mixing also influences degradation and preservation of biogenic components, pore-water concentrations of dissolved chemical species within the sediment mixed layer (Schink and Guinasso 1977; Berner 1980; Aller 1982; Alperin et al. 1999), microbial activity (Yingst and Rhoads 1980), and fate and transport of contaminants (Bothner et al. 1980; Officer and Lynch 1989).

In marine systems, both ^{210}Pb and ^{234}Th are continually produced within the overlying water column by their radionuclide parents, while ^{210}Pb is also supplied via atmospheric fallout. In freshwater systems, ^{234}Th may not be present, and ^{210}Pb supply may be dominated by the atmospheric fallout due the low abundance of the radionuclide parents within the water column. In either case once in the water column, ^{210}Pb and ^{234}Th interact with particles and are rapidly removed from dissolved to particulate phase. Due to the rapid adsorption onto particles, these elements along with other elements that rapidly become particle bound are referred to as “particle-reactive” elements. Once in the particulate phase, the particles to which they are attached may settle from the water column and be deposited at the sediment/water interface. The occurrence of excess

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^{210}Pb or ^{234}Th in the sediments deeper than would be produced by sediment accumulation alone can be used to characterize sediment mixing. While physical and biological mixing are separate processes, they may both occur within the same sediment column. However, most systems can be characterized as mixed by either dominantly physical or biological processes depending on the preservation of primary sedimentary structure. Physical mixing by waves, tides, and currents is generally event driven and potentially resets the sediment record within the mixing zone (Sanford 1992) while preserving sedimentary structure below the mixing zone. Biological mixing, referred to as bioturbation, is generally a steady-state process that can destroy the sedimentary structure (Dellapenna et al. 1998) depending on the mixing rate compared to accumulation rate. The radioactivity profiles of ^{210}Pb or ^{234}Th produced by sediment mixing are often used to calculate diffusion coefficients based on Fick's law of diffusion. The diffusion coefficient is defined as the rate at which the variance of particle location changes with time, where the variance is a measure of particle spread and is proportional to the squared velocity of the diffusing particle (Crank 1975). The coefficient units are length squared per unit time typically expressed as $\text{cm}^2\text{-yr}^{-1}$.

Most attempts to model sediment mixing have been used to evaluate biological mixing; however, the same models have been applied to physical mixing as well. The coefficients produced by biological mixing are referred to as biodiffusion coefficients although they are actually eddy diffusion coefficients. Biological sediment mixing is not truly a diffusive process; however, in many cases, biological mixing appears diffusive-like when many nondiffusive events are integrated over a short time period compared to the time scale of the radioactive tracer (Aller and Dodge 1974; Robbins et al. 1979; Boudreau 1986; Wheatcroft et al. 1990; Maire et al. 2008). If mixing is not rapid compared to the time scale of the tracer, tracer-dependent artifacts can appear (Reed et al. 2007; Lecroart et al. 2010). For a diffusion model to accurately represent the physical process of sediment mixing, sediment particles must be moved in a random manner over short distances. Large step length in the advection of sediment produced by conveyor belt-type sediment feeders may violate these assumptions. Nonrandom movement produced by selective feeding due to size, shape, texture, or composition may also violate these assumptions (Smoak and Patchineelam 1999). A one-dimensional biodiffusion model is the most commonly applied model due to its simplicity. Even though the assumptions may be violated and the model does not include realistic biological complexity, an accurate empirical model is produced in most cases. The fact that the model is used despite these issues has been referred to by Meysmann et al. (2003) as the "biodiffusion paradox." Other more complex and realistic models have been developed for different types of reworking using nonlocal transport models (Francois et al. 1997, 2001; Boudreau and Imboden 1987; Meysman et al. 2003; Maire et al. 2007). For a complete review of methods to quantify bioturbation rates, refer to Maire et al. (2008).

Sediment Mixing Model

Despite the fact that assumptions are often violated, sediment mixing is generally well described by a simple one-dimensional diffusion model based on Fick's law of diffusion. This is the most commonly used model to calculate diffusion coefficients. Activity (A ; dpm-g^{-1}) of the tracer in the sediment column will be affected by the sediment mixing (D ; $\text{cm}^2\text{-yr}^{-1}$), sediment accumulation (S ; cm-yr^{-1}), radioactive decay (λ ; yr^{-1}), and production (P ; $\text{dpm-g}^{-1}\text{-y}^{-1}$) of these radionuclides supported by their parents. All of these variables influence the observed tracer profile in the sediment column and are all included in the steady-state equation Eq. (1) presented by Guinasso and Schink (1975) where z is depth below the sediment-water interface.

$$D \frac{\partial^2 A}{\partial z^2} - S \frac{\partial A}{\partial z} - \lambda A + P = 0 \quad (1)$$

Using the excess activity allows the production term to be removed, and diffusion coefficients can be obtained from the following steady-state equation Eq. (2):

$$A_z = A_0 \exp\left(\frac{S - \sqrt{S^2 + 4D\lambda}}{2D} z\right) \quad (2)$$

In Fig. 1 Eq. (2) was used to create an idealized plot showing the activity of the tracer as a percent of the initial activity versus depth. In this plot the sediment accumulation rate is 2 mm-yr^{-1} , diffusion coefficient is $35 \text{ cm}^2\text{-yr}^{-1}$, and the mixed depth is 10 cm. The longer-lived tracer (i.e., ^{210}Pb) has a nearly vertical profile within the mixed layer, while the shorter-lived tracer (i.e., ^{234}Th) exhibits a strong gradient. In this case the ^{234}Th profile is dominated by mixing, and a simplified version of the equation Eq. (3) can be used to calculate the diffusion coefficient. This approach is commonly applied within the mixed zone by fitting a regression line to the activity profile of the tracer and using the gradient to calculate the diffusion coefficient (D).

$$D = \lambda \left[\frac{z}{\ln(A_0/A_z)} \right]^2 \quad (3)$$

In cases where accumulation and mixing rates are much slower, ^{210}Pb can be used in the same way ^{234}Th was used above to calculate diffusion coefficients.

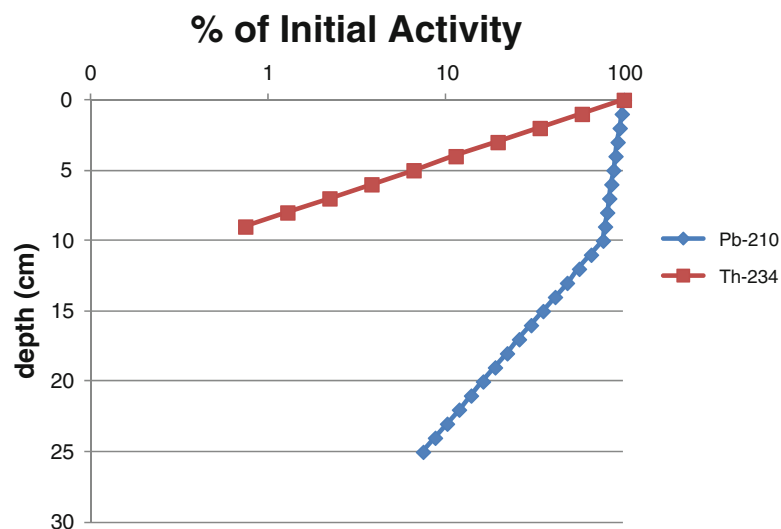


Fig. 1 Idealized plot showing the activity of the tracer as a percent of the initial activity versus depth (cm). Sediment accumulation rate is 2 mm-yr^{-1} , diffusion coefficient is $35 \text{ cm}^2\text{-yr}^{-1}$, and the mixed depth is 10 cm

Conclusion

Sediment mixing, either physically and/or biologically induced, results in the alteration of the original location of sediment particles. This sediment mixing, in turn, influences the degree of preservation of the sediment record and biogenic components, microbial activity, and fate and transport of contaminants. The most common approach to modeling sediment mixing is to use a one-dimensional diffusion-type model. The naturally occurring radionuclides ^{234}Th and ^{210}Pb are well-suited tracers to estimate the diffusion mixing coefficient in these models. When mixing is relatively rapid, the shorter time-scale tracer (^{234}Th) is the most suitable. When sediment accumulation and mixing rates are slower, the longer time-scale tracer (^{210}Pb) becomes more useful. While these models do not include all the complexity actually involved in sediment mixing, the models along with these uranium-thorium series tracers do create an accurate empirical representation of sediment mixing.

Cross-References

- ▶ [\$^{210}\text{Pb}\$ Dating](#)
- ▶ [Sedimentation Rate, Marine \(U-series\)](#)
- ▶ [U-Series Dating](#)

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Uranium-Lead, Diagenetic Processes

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Definitions

Diagenesis – Encompasses all of the processes that create and subsequently change sedimentary rocks after deposition of sediments and up to metamorphism.

Introduction

Uranium (U) has two long-lived isotopes, ^{238}U and ^{235}U , with very different half-lives, which decay through independent radioactive decay chains to lead (Pb), ^{206}Pb and ^{207}Pb , respectively. Because they represent two independent systems that should yield the same age, U–Pb dating (see ► [Uranium-Lead Dating](#)) can be a very powerful dating technique, particularly for detecting geochemical disturbance. Here we are concerned with how diagenesis impacts uranium and lead and particularly how this might impact the potential for U–Pb dating of sedimentary rocks. Our ability to use the U–Pb system for dating sedimentary rocks and/or diagenesis has everything to do with our ability to unravel the paragenesis of sedimentary rocks, as well as the stability of the minerals that might form through a paragenetic sequence. For example, loss or addition of the mineral components making up the rock and whether they contain significant uranium and/or lead dictate whether a meaningful age could be derived by U–Pb analyses. A first step is to consider the origin of sedimentary rocks.

U–Pb Dating of the Primary Constituents of Sedimentary Rocks

Sedimentary rocks can be clastic or chemical, and in terms of U–Pb dating, these present very different scenarios. Clasts are the solid particles derived from the breakdown of preexisting rocks, so an age of the particles in a clastic sedimentary rock would give the age of the parent rock (or perhaps an age that is meaningless if the U/Pb has been changed in those clasts). It is often the case that a variety of ages are produced, for example, in detrital zircon studies (see ► [Uranium-Lead, Detrital Zircon](#)). On the other hand, chemical sedimentary rocks that are formed as ions in solution are precipitated abiotically through oversaturation and/or through biogenic removal of the ions from solutions to create shells. If these chemical components are unaltered with respect to uranium and lead, and have high enough U/Pb ratios, a U–Pb age would give the age of formation, which would also be the age of deposition. A few studies have used U–Pb to date primary marine carbonate components such as fossils (Smith and Farquhar [1989](#); Smith et al. [1994](#); Getty et al. [2001](#); Denniston et al. [2008](#)). A major issue to be addressed with chemical sedimentary rocks is that

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they are vulnerable to later fluids which may alter the U/Pb and thus disturb the isotope systematics. In the worst case, this would produce a meaningless result; in the best case, it could give the age of the diagenetic alteration.

U–Pb Dating of the Fluids of Diagenesis

For both clastic and chemical sedimentary rocks, as the particles that will eventually be turned into rocks are deposited, the constituent minerals are initially subjected to the fluids they are deposited by and in. Through time and geologic processes, these particles and any subsequent phases that are created will be subjected to various other fluids that may be out of equilibrium with the rock and will therefore alter it. In the near-surface diagenetic realm, these fluids are seawater, meteoric water, and where fluids meet, mixing zones. Meteoric fluids, which result from atmospheric precipitation (rain or snow), are generally dilute and slightly acidic solutions that can therefore be very effective at dissolving labile constituents in exposed rocks, thus acquiring chemical signatures that reflect this interaction. As these fluids recharge aquifers, they continue to evolve chemically through interaction with the rocks they come in contact with. Through time, the meteoric fluids approach a chemical equilibrium with the host rocks, and they inherit isotopic and elemental ratios that reflect the integrated pathway. By the same token, the rocks these fluids interact with inherit isotopic and elemental ratios that reflect the fact that fluids have exchanged with them. Some examples of carbonates that are formed by meteoric fluids that have been dated by U–Pb are cave deposits such as flowstones and stalagmites (Richards et al. 1998; Polyak et al. 2008; de Ruiter et al. 2009; Cliff et al. 2010; Pickering et al. 2011; Woodhead et al. 2012; Woodhead and Pickering 2012; Bajo et al. 2012; Pickering et al. 2013) and paleosol (fossil soil) carbonates such as nodules and rhizoliths (Hoff et al. 1995; Winter and Johnson 1995; Rasbury et al. 1997; Wang et al. 1998; Leeder et al. 2008; Ludvigson et al. 2010). Lacustrine (lake) carbonates have also been shown to have good potential for U–Pb dating (Cole et al. 2005; Druschke et al. 2009).

Carbonate platforms are cemented early through marine cements. During some intervals of Earth history such as the Late Paleozoic, marine cements were aragonite and have high U/Pb ratios. Since aragonite is metastable and is not usually preserved in the rock record, it is important to consider how diagenesis will change the U/Pb ratio (Jones et al. 1995). In some cases, the time of formation of marine cements can be constrained by stratigraphic context and tested against other evidence for the age of the cements such as $^{87}\text{Sr}/^{86}\text{Sr}$ and correlation to dated ash horizons (Becker et al. 2002; Rasbury et al. 2004). When carbonate platforms form in arid environments, saline brines from behind the reef may flow through the buried parts of the platforms and diagenetically alter the carbonates, often forming dolomite. Because U and Mg are excluded from evaporite minerals, evaporated seawater can have high U/Ca and Mg/Ca ratios, producing a fluid that makes “hot” dolomite. Luczaj and Goldstein (2000) obtained U/Pb ages of dolomites from the Hugoton Embayment in the Midcontinent of the USA that were approximately 50 Ma younger than the depositional age of the lower Permian-aged carbonates that had been dolomitized. This study showed the hot dolomite was most likely produced by late Permian evaporative brines, consistent with the abundant late Permian salt that is found in that region.

As clastic sediments are buried, they are compacted and the waters within them are expelled and change through time as the conditions change. In the marine realm, we recognize early diagenesis as changes that take place before or during lithification. Nodules of various types, including phosphates, cherts, and carbonates, may form in this early diagenetic realm and their early formation is recognized by the bending of primary layering around them. One study examined

carbonate nodules with two distinct episodes of formation, both considered early diagenesis and showed that processes that could be called early diagenesis were separated by 35 Ma (Israelson et al. 1996). This is a fascinating view of early diagenesis and also a word of caution for assuming that anything appearing to be early diagenesis is effectively the time of sedimentation.

As sediments are buried, fluids that were trapped within the sediments at the time of sedimentation, for example, seawater, can be squeezed out through compaction, possibly resulting in the dissolution of unstable phases and/or the precipitation of new minerals and eventually turning the sediments into rocks, through processes that are collectively termed lithification. Because these fluids are far from the surface, they are typically low in dissolved oxygen. Iron and manganese are soluble in low-oxygen (reducing) fluids, so geochemists use the presence of these elements in carbonate cements as a way to demonstrate that the cements formed from burial fluids. In addition the presence of iron and manganese in primary constituents such as fossil shells is used as an indication that the shells are diagenetically altered and therefore would not necessarily provide information on the primary fluid. Burial fluids migrate in directions that are controlled by the permeability of the rocks as well as through the influence of hydrologic head, interacting with the rocks and acquiring isotope and element ratios that reflect the integrated interaction pathway. In some cases burial fluids from one formation could mix with fluids from other diagenetic realms, creating a new fluid out of equilibrium with the rock with potential for more diagenetic change. Finally, these resulting rocks may be uplifted through tectonic stresses and perhaps faulted and fractured in the process. This changes the hydrologic head, allowing meteoric fluids to permeate downward and higher temperature burial fluids to move up through the rocks, perhaps facilitated by the fractures that have been created. These changes in hydrology can result in fluid mixing which may produce corrosive fluids that dissolve some constituents and in other cases causing phases to precipitate as fluids become oversaturated and form cements. Veins and geothermal deposits that result from such tectonic events have been dated by U-series disequilibrium (Uysal et al. 2007, 2009, 2011; Nuriel et al. 2012a, b), and there is every reason to believe examples from more ancient tectonic events beyond the range of U-series dating could be dated using U–Pb. This is a frontier in the Earth Sciences. Additionally this renewed tectonic activation could be accompanied by volcanic activity with hot plutonic bodies providing a source of heat that promotes fluid circulation through the rocks, sometimes producing ore deposits. U–Pb dating of carbonates associated with the ore deposits would date the time of ore formation and provide valuable insights into the process(es) responsible for economic deposits (Brannon et al. 1996; Grandia et al. 2000).

Summary: U–Pb Dating of Sedimentary Rocks and Diagenesis

It is often possible to decipher the diagenetic history of a sedimentary rock through petrographic and geochemical investigation. Clastic rocks may have cements that formed early, even during initial deposition, or later through compaction and burial and may have even later crosscutting veins resulting from tectonic processes. Whole-rock analyses of such a rock would give a U/Pb result that is a mix of these processes and would not likely give a meaningful U–Pb age. However, if one could separate out generations of cements based on careful petrographic analyses and if these cement generations had not been altered since formation and have high enough U/Pb ratios to have produced measurable radiogenic Pb, it would be possible to date the diagenetic events. While the application of U/Pb to dating diagenetic phases in clastic sedimentary rocks is rare, numerous studies have investigated other geochemical constraints such as fluid inclusions and oxygen isotopes which can be used to place bounds on the temperature and salinity of the fluids. These phases

are often quite small, on the order of tens of microns, but as techniques such as laser ablation MC-ICP-MS (Multi-Collector Inductively Coupled Plasma Mass Spectrometry) and SIMS (Secondary Ion Mass Spectrometry) continue to be developed, it is likely that U–Pb dating of these phases will offer important insights that have otherwise had to be inferred as to the process(es) of clastic diagenesis. Imagine the potential for understanding the geologic processes a rock has experienced if, in addition to temperature and salinity, one could also date the generations of cements that are recognized in a paragenetic study. This is a frontier in the Earth Sciences.

The major difference between clastic and chemical sedimentary rocks is that the initial constituents for clastic rocks have an inherited history, while newly formed chemical constituents in chemical sedimentary rocks, if unaltered, will give the age of deposition if they have high enough U/Pb ratios to be dated. After deposition, these chemical constituents also experience diagenesis to eventually become a rock, with unstable phases dissolving or being replaced and various cement phases and crosscutting veins influencing the U–Pb system in a similar manner as we discussed for clastic sedimentary rocks in the preceding paragraph. That is to say, in order to become a rock, we can imagine that all sediments have experienced multiple diagenetic realms with fluids that have different U/Pb which may dissolve some phases and precipitate others perhaps further down the path of fluid-rock interaction. These changes will alter the U–Pb systematics making it impossible to obtain a meaningful age through whole-rock analyses. However, if individual phases can be sampled, and this is increasingly being used particularly in carbonate rocks, a meaningful age of the new phases may be obtained which will allow geologists to date the timing of that event, not the rock.

Through geologic time, a rock is likely to have been exposed to multiple diagenetic fluids resulting in dissolution and precipitation of various minerals as well as solid-state exchange with others and thus producing a complex array of isotope and element ratios. It is in this framework that diagenesis of U–Pb must be considered. Sampling for U–Pb dating should target phases that can be recognized petrographically and can be put in a paragenetic framework. In this way, the system becomes even more powerful with the potential not only to date the time of deposition but also to date diagenetic events that postdate deposition.

Cross-References

- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)

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Uranium-Lead, Zircon

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Definition

Uranium-lead: Long-lived radioactive isotopes of uranium (^{235}U and ^{238}U) decay to stable lead (^{207}Pb and ^{206}Pb , respectively) at a rate, which is constant but different for the two systems. The ratio of accumulated lead to remaining uranium is a function of time and is a direct measure of the time of formation of minerals and rocks.

Zircon: A mineral consisting principally of zirconium, silicon, and oxygen and with trace amounts of uranium.

Main Characteristics of Zircon

Zircon is an orthosilicate with a tetragonal crystal structure and the chemical formula ZrSiO_4 . It occurs as euhedral to prismatic crystals of various elongations but also as grains with subrounded anhedral shapes due to resorption and grinding during metamorphic and/or sedimentary reworking (see Fig. 1). The mineral has a hardness of 7.5 and a density of 4.7 g/cm^3 , decreasing to 3.9 in heavily radiation-damaged (metamict) grains. Uranium is incorporated in the crystal in trace amounts (zero to several thousand parts per million) by replacing zirconium, which has a similar ionic radius and equal valence (+4). Other important trace elements are hafnium (1 %), thorium, yttrium, phosphorus, and the heavy rare earth elements.

Behavior of Zircon During High-Temperature Geological Processes

Zircon grown in slowly crystallizing magma chambers commonly exhibits regular growth zoning defined by alternating layers of slightly different chemical composition (see Fig. 2). This regular layering can be disrupted and modified by recrystallization processes leading to very complex internal textures. Zircon can survive partial melting processes and remain as a core, entrained from the source of the magma, inside new magmatic crystals. Protracted high-temperature metamorphic processes can recrystallize zircon expelling part of the accumulated lead. This process can be accompanied by growth of new layers of metamorphic zircon.

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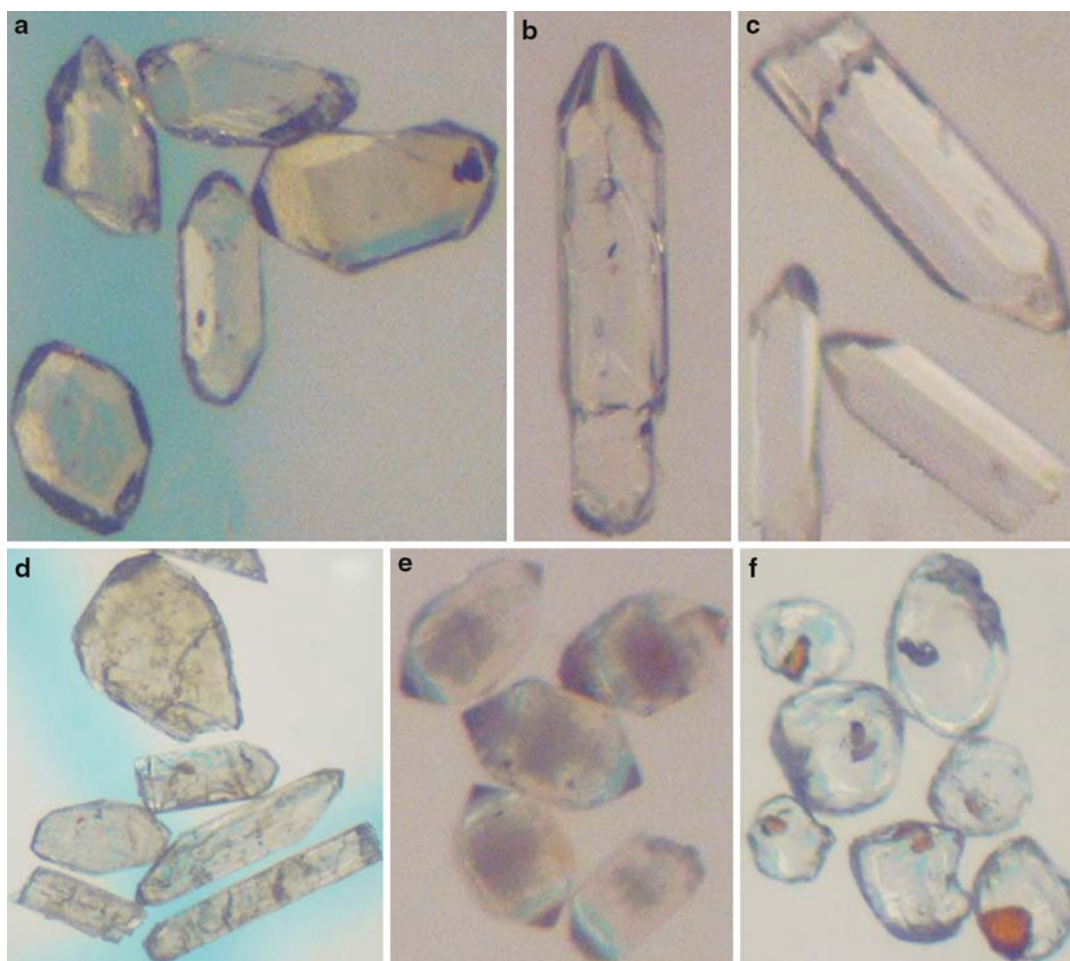


Fig. 1 Typical morphologies and other properties of zircon in common rocks. (a–c) Euhedral, colorless zircon with variable degrees of elongation; (d) euhedral zircon, prismatic and flat, locally turbid and fractured; (e) short-prismatic euhedral zircon with clear outer zones enclosing a cloudy, opaque core; (f) subrounded zircon of metamorphic origin with inclusions of coeval rutile. The grains are approximately 100–300 μm in size

Role of Zircon for U–Pb Dating

Zircon is the mineral most widely used for determining geological ages with the U–Pb system. The main reasons are (1) the incorporation of variable amounts of uranium, but essentially no lead, at the time of formation, so that virtually all the lead found in a grain of zircon today stems from the radioactive decay of uranium; (2) the very widespread occurrence of zircon in many different rock types; and (3) the resistance of zircon during weathering processes, metamorphic transformations, and melting of the host rocks (Hanchar and Hoskins 2003).

A further advantage for dating stems from the existence of two decay series in the uranium-lead systems. These two series run at different speeds, yielding two ages for the same dated object. If the two ages are equal, they prove that the mineral has remained a closed system and did not lose or gain Pb or U since the time of formation. If the two ages do not match, the system must have been open at some point, and the apparent ages have no immediate geological meaning.

Zircon requires no, or just marginal, corrections for initial lead, avoiding therefore a major source of uncertainty. For this reason, it is possible to achieve much higher precision for zircon than for most other uranium-bearing minerals. Modern isotope dilution thermal ionization mass

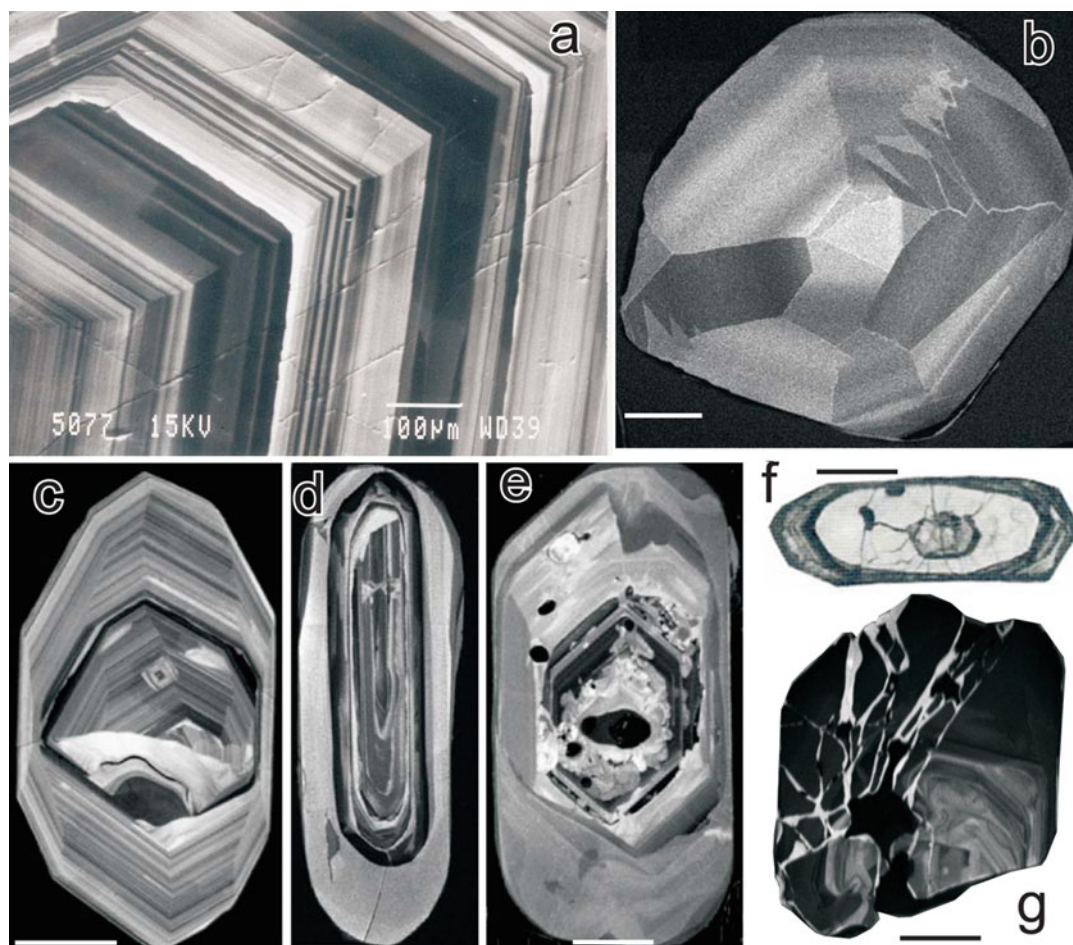


Fig. 2 Cathodoluminescence images of sectioned and polished zircon crystals – *bright zones* have low uranium contents, whereas *dark areas* are richer in uranium. (a) Regular growth zoning, but with some local discontinuities indicating resorption episodes in a magma; (b) zircon with sector zoning – a common appearance of zircon grown under high-temperature metamorphic conditions; (c) zircon crystal with very well-developed growth zoning, except for an internal zone with an irregular overprint indicating resorption and recrystallization; (d) interior of zircon with regular growth zoning surrounded by a broad rim of more uniform composition; (e) zircon crystal with internal convolute zoning; (f) zircon crystal with multiple growth zones – the internal part of a xenocrystic core is richer in uranium than the rims, its decay and volume expansion leading to fracturing of the surrounding layers; (g) zircon with regular growth zoning superimposed by a later crack-seal texture (Images courtesy of Sven Dahlgren, Alfred Kröner, and Kosuke Ueda)

spectrometry (ID-TIMS) can achieve precisions on the ages of better than 1% and resolve the timing of very complex geological processes (e.g., Schaltegger et al. 2009; Schoene et al. 2010; Wotzlaw et al. 2012).

The onlapping of multiple zones, reflecting growth or reworking at different times during the history of a zircon population, provides the opportunity to use composite grains or composite zircon populations to date such multiple events (e.g., Harley et al. 2007). Complex zoning, however, can also make the dating process very difficult in those cases where analysis represents mixed ages, possibly further complicated by superimposed lead loss effects.

Most applications of this method are oriented toward the determination of the time of magmatic or metamorphic crystallization of rocks, but zircon can also be used to study provenance of

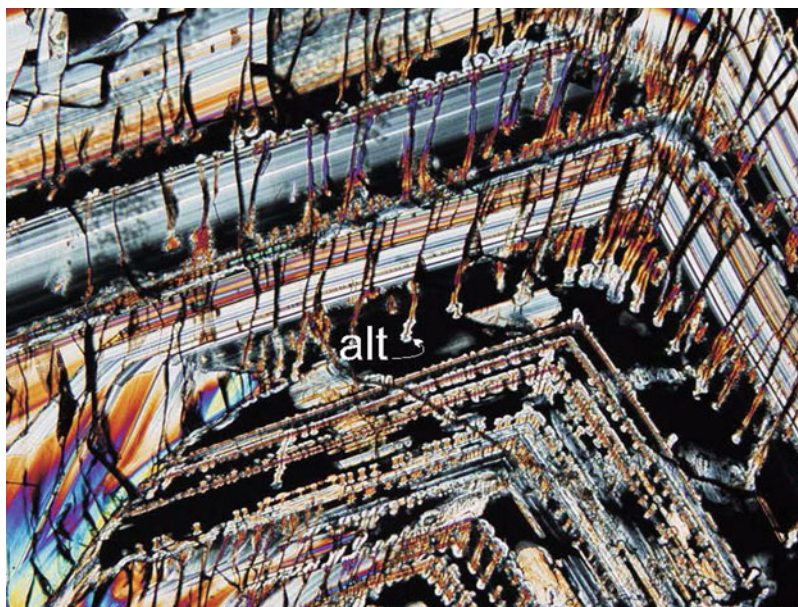


Fig. 3 Detail of a zircon section showing regular growth zones that have become metamict with time. Those with more uranium (showing *low luminescence*) have expanded and fractured the zones with less uranium, less metamict (*brighter luminescence*), and more brittle. Fluids intruding along the fractures have developed alteration haloes (*alt*) that propagate into and change the metamict material (A full description is given in Nasdala et al. 2010; photograph courtesy of Lutz Nasdala, University of Vienna)

sedimentary rocks and constrain their time of deposition, or it serves to correlate strata linked to meteorite impact events (e.g., Kamo et al. 2011).

Effect of Radioactivity on the Structure and Behavior of Zircon

For each series, the radioactive decay of uranium (and thorium) emits 6–8 alpha particles, each accompanied by a recoil of the nucleus. This process destroys few nanometers of the crystal lattice of zircon around the decay sites. With time, the accumulation of radiation damage leads to an increase in the volume and a reduction of the density of the zircon, together with other physical and optical changes. Because zircon commonly consists of concentric zones with alternating, variable uranium contents, the expansion of uranium-rich zones stresses and eventually fractures the uranium-poor, and still crystalline, layers. The fractures create pathways along which fluids can penetrate in the crystal and cause chemical changes, including the removal of lead (see Fig. 3). Because the remaining uranium still resides in healthy lattice sites, loss of uranium is less likely than loss of lead.

Newly formed zircon crystals are colorless and transparent. With the increasing accumulation of radiation damage, which is proportional to U content and age, the zircon becomes gradually more colored, first pink, then red or brown and translucent, and eventually dark or white and opaque, the latter especially in chemically altered domains.

Strategies to Counter the Effects of Radiation Damage When Dating Zircon

In order to obtain geologically valid ages, it is important to avoid or minimize the use of zircon grains that have lost lead. This can be achieved first by selecting grains, or parts of grains, which are free of fractures and turbid domains. Zircon analyzed by isotope dilution thermal ionization mass spectrometry (ID-TIMS) can be initially treated by air and/or chemical abrasion. In the air abrasion treatment (Krogh 1982), the grains spin around inside a steel chamber by means of a jet of compressed air abrading away the outside layers, breaking fractured grains, and polishing them to remove the most radiation-damaged and radiation-altered parts of the grains and reduce the extent of lead loss. Chemical abrasion (Mattinson 2005) involves two stages. In the first stage, the grains are heated to 900–1,000 °C, annealing the parts of the zircon with a low amount of radiation damage, but not the most heavily damaged domains. In the second stage, the grains are immersed in hydrofluoric acid at 180–200 °C for 10–20 h, dissolving the most radiation-damaged parts of the grains but not affecting uranium and lead in the remaining crystalline parts of the zircon.

Zircon analyzed by ion probe or laser ablation inductively coupled plasma mass spectrometry is normally sectioned and polished and then examined using cathodoluminescence or backscatter electrons in order to identify optimal target areas (with diameters between 10 and 60 µm), which are free of alteration, fractures, or inclusions and suitable for uranium-lead analysis.

Because of the existence of the two parallel decay chains ^{238}U to ^{206}Pb and ^{235}U to ^{207}Pb , it is generally possible to recognize biased data reflecting the analysis of isotopically disturbed zircon (“discordant” data) and to extrapolate data for cogenetic zircon affected by variable amounts of lead loss to the “true” age of formation of the system.

Summary

The mineral zircon is an efficient geochronometer because of its widespread occurrence, resistance to destruction and isotopic resetting during magmatic or metamorphic events, incorporation of uranium but no initial lead at the time of formation, and its combination with the two chains of ^{238}U and ^{235}U , which operate at different rates while decaying to ^{206}Pb and ^{207}Pb , respectively. The main difficulty in dating zircon is related to the gradual accumulation of radiation damage, which destroys the zircon lattice, causes fracturing, and permits access to fluids, which leach out lead and bias the ages. Some of the most essential tasks involved in zircon dating are the identification of multiple generations of zircon in a population and the ability to isolate and analyze separately domains that have escaped loss of lead.

Cross-References

- [Geochronology](#)
- [Geological Time Scale](#)
- [Jack Hills Zircon](#)
- [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- [Mass Spectrometry](#)
- [Radiation and Radioactivity](#)
- [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- [Thermochronology, Detrital Zircon](#)

- [Uranium-Lead, Chemical Isochron U-Pb Method \(CHIME\)](#)
- [Uranium-Lead, Detrital Zircon](#)
- [Uranium-Lead, Hydrothermal Events](#)
- [Uranium-Lead, Igneous Rocks](#)
- [Uranium-Lead, Metamorphic Rocks](#)
- [Uranium-Lead, Rubidium-Strontium, Kimberlite](#)

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Dendrochronology, Volcanic Eruptions

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Synonyms

[Dust veil](#); [Extrusive volcanism](#); [Tephra deposition](#)

Definition

Dating of events associated with volcanism that leaves a permanent marker in tree-ring records. Such events include air temperature cooling, deposition of ash layers, lava flows, and magmatic degassing.

Introduction

The geological applications of dendrochronology cover a wide range of topics, from paleoseismology (Jacoby 1997) to paleovolcanism and its effects on climate (Zielinski 2000). With specific regard to volcanic eruptions, tree-ring records have been used in multiple ways to date events associated with explosive and effusive volcanism, including magmatic degassing. Because wood formation is influenced by environmental factors (Plomion et al. 2001), tree species that are directly or indirectly impacted by volcanic eruptions can record such events in their growth layers. Datable volcanic effects on woody species range from annihilation (death dates) to rebirth (establishment dates) but also include growth changes in surviving trees (Yamaguchi 1993). Such changes can be abrupt, hence only detectable in single rings. These individual growth layers can be very small (“microrings”), down to the point of not being present (“locally absent rings”) in one or more samples collected at a site (Biondi et al. 2003). Individual tree rings that are typically not so small can show anatomical damage from freezing (“frost rings”) in response to the sudden reduction of sunlight and its associated air temperature drop, caused by volcanic dust veils (LaMarche and Hirschboeck 1984). Depending on the type of extrusive materials (tephra deposition, lava flows, emission of sulfuric gases, etc.), surviving trees can present gradual, rather than abrupt, changes over multiple consecutive years. Such departures from previous tree-ring patterns can be positive (increased growth, or “release”) or negative (decreased growth, or “suppression”). The diversity of volcanic effects on trees depends on the variety of materials that can be ejected, as well as on the location, species, size, and age of the trees, together with other site conditions, from elevation and topography to vegetation features. On one hand, such richness of potential information has generated a long tradition of tree-ring applications to volcanology. On the other hand, the difficult task of identifying what, when, and how trees were impacted by specific past volcanic events has caused multiple, heated, and prolonged scientific debates.

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Historical Development

Modern dendrochronology, which is the study of past changes recorded by wood growth, is based on the rigorous application of Crossdating techniques to assign calendar dates to tree rings (Fritts and Swetnam 1989). When so defined, this branch of science was established in the western United States at the beginning of the twentieth century by Andrew E. Douglass, an astronomer at the University of Arizona in Tucson (Webb 1983; Nash 1999). Tree-ring dating is closely connected with the study of wood formation, and relevant studies, for example, on the anatomy of frost rings (Rhoads 1923), also date back about a century. On the other hand, while the hypothesis that exceptionally cold years could be caused by volcanic eruptions is found in Benjamin Franklin's (1785) writings, the global atmospheric radiative effects of volcanic aerosols could only be tested with the advent of satellite and remote sensing technology in the 1980s (Ramanathan 1988). At about the same time, the Volcanic Explosivity Index, or VEI (Newhall and Self 1982), was introduced to describe the magnitude of past explosive eruptions in a semiquantitative manner. Impacts of extrusive eruptions on tree rings at sites located near a volcano were first described in the 1960s, but sample sizes were small (i.e., less than ten trees), ring boundaries were uncertain either because of poor sample preservation and surfacing (Druce 1966) or because of species growth patterns and anatomical features (Eggler 1967), and no crossdating was used. A notable exception was the A.D. 1064–1065 dating of Sunset Crater, Arizona (Smiley 1958), where a larger number of samples from archaeological ruins were investigated and tree-ring dates were assigned by crossdating. On the other hand, less than ten trees showed a distinct growth reduction after 1064, and nonvolcanic disturbances can cause similar effects in ring widths of the same species in this geographical area (Sheppard et al. 2005).

A major catalyst for dendro-volcanology came from the 1980 eruption of Mount St. Helens in the Pacific Northwest region of the USA. The blast that occurred on May 18 of that year with an estimated VEI of 5 (the maximum is 8) removed the top 400 m of the mountain and rose to 24 km into the stratosphere (Brantley and Myers 2000). It was the deadliest and most economically devastating volcanic event in United States history, exceeding a billion dollars in damage. A total of about 60 people, including a volcanologist, and more than nine million cubic meters of valuable timber were among the losses suffered over the nearly 600 km² ravaged by the eruption (McLean and Lockridge 2000). Several studies were published shortly thereafter on tree growth responses to the eruption (Mahler and Fosberg 1983; Hinckley et al. 1984) and on dendrochronological dating of previous events (Yamaguchi 1983, 1985). The enhanced interest in past volcanic histories, and the realization of potential long-range temperature effects from volcanic dust veils, prompted an extensive study of frost rings in the wood of high-elevation bristlecone pines (LaMarche and Hirschboeck 1984). Another anatomical feature, i.e., the “light rings” caused by reduced latewood formation in conifers growing at high elevations or latitudes, was investigated for their potential connection with reduced temperatures associated with volcanic eruptions (Filion et al. 1986). Extensive networks of tree-ring sites, whose analysis was then facilitated by advances in computational power and numerical processing, became the target of sophisticated statistical methods to detect changes in tree-ring-reconstructed climatic variables that could be linked to volcanic eruptions (Lough and Fritts 1987).

Yet another method of tree-ring analysis, X-ray densitometry (Polge 1970) had come of age in those decades (Schweingruber et al. 1978), and networks of tree-ring sites sampled in the late 1970s and early 1980s were analyzed using this new technique (Schweingruber et al. 1991). Subsequent research to date has continued to employ the tools elaborated in previous years, from light rings (Szeicz 1996) to densitometry (Jones et al. 1995), expanding the number of sampled sites (D'Arrigo

and Jacoby 1999) as well as the geographical (Hantemirov et al. 2004) or temporal (Salzer and Hughes 2007) range of previous studies, and applying increasingly complex numerical treatments for identifying volcanic signals in tree-ring proxy records (Breitenmoser et al. 2012). As an alternative to the exhaustive filtering and massaging of large spatiotemporal datasets, other studies in the past few decades have investigated the use of chemical markers in tree rings linked to volcanic eruptions (Pearson et al. 2009), including magmatic degassing in the absence of explosive events (Biondi and Fessenden 1999).

Basic Principles and Applications

Trees and other woody plants grow by covering themselves with a new layer of tissue every year (Larson 1994). When seen on a transverse section, such wood layers appear as concentric tree rings. Because tree growth is influenced by the environment, tree rings are then natural archives of past environmental conditions. For instance, less wood is formed near the base of a tree stem when climate conditions are less favorable, producing narrower rings (Speer 2010). If an eruption takes place, trees growing close enough to the volcano can be scorched by hot gases or covered with tephra and may either be killed or survive depending on their species, age and vigor, microsite conditions, as well as the chemistry and temperature of the gases and the thickness and coarseness of the tephra layer (Segura et al. 1994). Surviving trees typically experience abrupt suppression of radial growth (Hinckley et al. 1984), including locally absent rings (Yamaguchi and Hoblitt 1995). This immediate decline can be followed by a prolonged period of reduced radial increment (Segura et al. 1995) or by its opposite, i.e., greater than normal growth rates, often in connection with concurrent stand dynamics and resulting competitive interactions (Abrams et al. 1999).

Major explosive volcanic eruptions that inject dust and aerosols into the stratosphere are capable of causing large-scale surface cooling (Minnis et al. 1993). Distant, large-scale networks of tree-ring chronologies from temperature-limited sites can reflect those eruptions in anatomical xylem features, such as frost damage (D'Arrigo et al. 2001) or reduced latewood formation (Jacoby et al. 1999). Freezing damage to coniferous species causes the formation of deformed and collapsed xylem cells depending on the intensity of the frost, the degree of cambial activity at the time of the temperature drop, the tree species and size, and possibly other factors (Day and Peace 1934). Frost rings have been reproduced experimentally (Glerum and Farrar 1966), and their cross-sectional features are clearly distinguishable on a well-prepared wood sample at the magnification (10–50×) normally used in tree-ring studies. While crossdating among a large enough number of samples guarantees accurate dates, the year assigned to a frost ring may have some uncertainty if the injury occurs at a ring boundary, so that it could represent either a late frost in a year or an early frost in the following year. This situation is more frequent as ring widths become smaller (<0.1 mm), but using well-dated frost rings to resolve uncertain cases leads to potential bias and should be either avoided or well documented. With regard to “light rings”, the reduced cell wall thickening in latewood that causes their name also causes minimal density and can be caused either by low air temperature or by insect defoliation (Liang et al. 1997).

Measured annual growth parameters, such as ring width (Fritts 1976) or maximum latewood density (Briffa et al. 1988), are routinely used for dendroclimatic reconstructions. When wood formation is limited by air temperature, as it is usually the case for trees located at high elevations or high latitudes (D'Arrigo et al. 2006), dendrochronological parameters can reflect a volcanic cooling, thereby providing a record of past eruptions (Briffa et al. 1998). Chronologies developed from ring widths present a greater amount of time-series autocorrelation (or “persistence”) than chronologies

generated from annual density peaks (called maximum latewood density, or MLD), which also tend to reflect growing season conditions rather than integrating environmental signals over multiple years (D'Arrigo et al. 1992). Therefore, it is normally assumed that the temporal lag between volcanic cooling and its incorporation in tree-ring proxy records increases going from frost rings to light rings and from maximum latewood density to ring width chronologies (D'Arrigo and Jacoby 1999).

The main application of dendrochronology to volcanology is the definition of impacts on ecosystems and on human societies, either current, past, or long lost. Besides providing information on ecological processes in forests, tree-ring records of volcanic eruptions contribute to estimating the past frequency of destructive events. This numerical datum can then improve the definition of potential risks, especially with regard to explosive phenomena occurring at short intervals from one another (Yamaguchi 1985). At the same time, because of possible global impacts of volcanoes on climate (Robock and Mao 1995) and biogeochemical cycles (Krakauer and Randerson 2003), well-dated records of past eruptions are needed to improve the accuracy of models used to generate future scenarios linked to anthropogenic emissions of greenhouse gases (Ramanathan 1988). As any other dating tool, tree-ring records of volcanic eruptions can alter historical interpretations simply by changing the order of events. While dates are not by themselves reason for cause-and-effect relationships, they are able to negate theoretical ones as no effect can precede its hypothesized cause.

Current Controversies and Knowledge Gaps

Major volcanic eruptions have been dated using other types of records, from dust layers and chemical properties in ice cores (Larsen et al. 2008) to archaeological and written sources (Stothers 1999). Not all records agree, and in particular, dates assigned to some major eruptions using geochemical markers in Greenland ice cores (Vinther et al. 2006) are currently in disagreement with tree-ring records (Baillie 2010). A particularly important event is the Minoan eruption of Thera, an island in the Aegean Sea now called Santorini, which took place in the mid-second century BC. The date of this volcanic time marker is of critical importance for the stratigraphic and archaeological synchronization of ancient Eastern Mediterranean societies, the cradle of western culture. The eruption, which left a caldera and ash deposits up to hundreds of meters in size, has been linked with the collapse of the Minoan civilization on the island of Crete, 110 km to the south, possibly spurred by gigantic tsunamis. The controversy has lasted for decades, with historical/archaeological dates centered in 1550–1500 BC (Wiener 2009), tree-ring records pointing to 1629–1627 BC (Baillie 2010), ice-core geochemistry focused on 1642–1641 BC (Vinther et al. 2006), and radiocarbon dates spread over 1683–1611 BC (Manning et al. 2006). Each of these sources of evidence has strengths and weaknesses. As an example, radiocarbon dating of an olive branch from the eruption site provided a date range of 1627–1600 BC (Friedrich et al. 2006), but it is difficult to determine if the sample was dead or alive at the time of the eruption (Wiener 2010), and wood anatomical features make any ring analysis problematic for this species (Cherubini et al. 2013).

The chemical signature of volcanic eruptions has been proposed as a possible tool for testing the accuracy of tree-ring dates assigned to individual events (Pearson et al. 2005). Because elemental concentrations can vary considerably in the same tree both around the stem and at various heights in the trunk (Watt et al. 2007), clear evidence needs to be presented that specific chemical signals are replicable across samples from the same tree as well as from different trees of the same species and site (Kirchner et al. 2008). When crossdated ring sequences are combined with localized information on geochemical variables, a high degree of accuracy and confidence can be placed in the dating

(Sheppard et al. 2008). This, for instance, was the case with regard to the onset of magmatic degassing in forest stands of the Sierra Nevada, which produced abrupt changes in crossdated ring-width sequences (Biondi and Fessenden 1999) and in their radiocarbon concentrations (Cook et al. 2001).

A number of confounding factors hamper the use of proxy records for dating volcanic eruptions. Several of these factors can be categorized as false positives or false negatives (Cleland 2002). Considering anatomical markers in tree rings, not all of them are related to major volcanic eruptions (false positives), and known major volcanic eruptions took place without producing such markers (false negatives). In addition, not all cold summers over a region are related to volcanic events, and not all volcanic years produce a cold summer at the majority of sampled sites in a tree-ring network (D'Arrigo et al. 2013). Depending on the prevailing climate regime and ecological requirements of a species, climate-driven responses to major eruptions can even favor tree growth rather than depressing it. Such inverse response was proposed for Thera because the potentially cooler summers generated by the dust veil would have reduced evapotranspiration, resulting in 2–3 years of abnormally high growth in woody species adapted to the normally dry Mediterranean conditions (Kuniholm et al. 1996). These hypothetical responses, albeit reasonable, require further testing, which is best attained using detailed ecophysiological and anatomical studies at sub-monthly time scales (e.g., Rossi et al. 2013). Finally, when evaluating unusual episodes within a time series, it is best to employ a quantitative approach, such as ranking episode features (duration, magnitude, peak) according to predefined numerical criteria (e.g., Biondi et al. 2008).

An additional wrinkle in the protracted debate over tree-ring reconstructions of volcanic eruptions has recently emerged. Climate modelers have tried to reconcile their simulations of regional and global climate impacts from volcanic eruptions by postulating that tree-ring chronologies for northern latitudes or from high elevations are all consistently missing, and in more than one occasion, a year of growth (Mann et al. 2012). The ensuing vigorous responses (Anchukaitis et al. 2012; D'Arrigo et al. 2013; Esper et al. 2013) have concentrated on choices made when modeling tree-ring formation and on correlations with instrumental or proxy records, showing a general disruption of these statistical relationships when tree-ring chronologies are shifted by one or more years. The essential question underlying the debate is the likelihood that collections of tree-ring samples from a single site, or even from multiple sites in a region, would fail to include a year's growth. The frequency of locally absent rings increases in semiarid environments as a response to drought, but existing tree-ring collections pooled by latitude, species, or elevation include a percentage of "missing" rings that does not exceed 10 % (St. George et al. 2013). A number of other issues have been raised, starting from how evidence deteriorates going further and further back into the past. For relatively recent events, such as the 1815 explosion of the Tambora volcano (Stothers 1984), there is no chance of a universally missing ring given the large number of available proxy and instrumental records. For earlier eruptions, on the other hand, even their dates become less reliable as temporal separation increases (Plummer et al. 2012).

Historical archives and environmental records of past events are notoriously open to multiple interpretations, but so are model outputs and their underlying assumptions. From a tree-ring perspective, not all is known about the environmental conditions required for, and the biological mechanisms leading to, wood formation in areas where long proxy dendroclimatic records have been developed. Anatomical and ecophysiological studies have the potential to uncover such mechanisms without complex numerical analyses (Fonti et al. 2010; Rossi et al. 2012). On the other hand, the impossibility of experimental testing on past events (Biondi 2013), when combined with lack of self-criticism or doubt, could maintain the striking tendency to robust bragging that has become a distinguishing trait of high-profile articles on volcano-climate-proxy records connections.

Summary

Dendrochronological studies of volcanic eruptions employ a variety of techniques, from anatomical to statistical, for detecting the signals left by past events in tree-ring records. When large datasets composed of multiple sites and species are independently analyzed, the resulting tree-ring dates assigned to past events are more reliable than those derived from other proxy records or from modeling exercises. Dendrochronological dates are exact when sufficient sample replication exists, but the correct interpretation of environmental signals, including volcanic ones, that are embedded in wood anatomical markers and growth patterns requires careful consideration of alternative, competing hypotheses.

Cross-References

- ▶ [14C Dating](#)
- ▶ [Dendrochronology, Dwellings](#)
- ▶ [Dendrochronology, Fire Regimes](#)
- ▶ [Dendrochronology, Palaeoclimate](#)
- ▶ [Dendrochronology, Surficial Processes](#)
- ▶ [Dendroentomology](#)
- ▶ [Geochronology](#)
- ▶ [Tephrochronology](#)

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Luminescence, Glacial Sediments

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Definition

Glacial	Of, or pertaining to, ice masses of sufficient magnitude that they are able to deform under their own mass.
Glacial sediments	Detrital lithic materials deposited as a result either of direct glacial movement, such as a diamict, or an indirect consequence of glacial processes, such as fluvioglacial sediments.
Luminescence dating	The use of the luminescence signal emitted from a mineral for dating. For geological sediments, the event being dated is the last exposure to daylight, and this normally corresponds with deposition of the sediment.

Introduction

Luminescence dating of sediments associated with former glacial activity has been undertaken for over 40 years. Some of the earliest work undertaken on the application of luminescence to dating geological sediments was carried out in the former Soviet Union and included analysis of sediments resulting from a variety of different glacial processes. This work was not widely known outside the Soviet Union (see “► [Luminescence Dating, History](#)”), and in later reviews (e.g., Dreimanis et al. 1978; Wintle and Huntley 1982), it was criticized for some important errors.

A major challenge that has been common to all luminescence studies of glacially derived sediments is assessing whether they were exposed to sufficient light at deposition to reset the signal used for dating. Early work used thermoluminescence (TL) signals, and a great deal of effort was expended trying to assess what proportion of the TL signal remained at deposition so that ages could be calculated. Optically stimulated luminescence signals (OSL) tend to be reset by exposure to daylight more rapidly than TL, and when these methods became available, they were rapidly adopted for analysis of glacial sediments.

There are many different types of glacially derived sediments, and the likelihood of exposure to daylight prior to deposition varies considerably. It is clear that selection of depositional facies where exposure to daylight at deposition is most likely is important. The most suitable environments are probably those involving fluvioglacial or fluviolacustrine processes, though in both cases shallow water facies are much preferable to deepwater ones.

For some glacial sediments, OSL methods can be applied in a relatively straightforward manner, while in environments where the exposure to daylight is more limited, complex methods involving measurement of single grains are required in order to be able to identify the small proportion of grains within the sample that did receive sufficient daylight exposure to reset their signal and hence

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give an accurate age. Recent reviews of the application of OSL methods to glacially related sediments are provided by Fuchs and Owen (2008) and Thrasher et al. (2009).

History

The limited exposure of many types of glacially derived sediments to daylight was realized in early studies that studied the thermoluminescence (TL) signals. A great deal of work was undertaken to try to define the extent to which these TL signals were reset. Gemmell (1988) studied the change in the TL signal of suspended sediment collected along a 4 km long reach of a channel draining the base of the Austerdalsbreen glacier in Norway. Although he could observe that the TL signal decreased with distance downstream of the glacier, this decrease was irregular because of the incorporation of older material from the banks of the channel. Forman (1988) chose to study a range of different depositional environments around glaciers in Spitsbergen and found that tills and ice-proximal glaciomarine sediments appeared to have been exposed to light the least, while littoral and ice-distal marine sediments had been exposed for the longest. These studies of proximal glacial sediments implied that it was not possible to obtain accurate luminescence ages using TL methods.

Optically stimulated methods, both using visible (optically stimulated luminescence, OSL) and infrared stimulation (infrared stimulated luminescence, IRSL), were introduced in the 1980s and 1990s. They measure signals that are reset more rapidly by exposure to daylight than TL and thus may be more suitable for dating glacial sediments where exposure to daylight at deposition is limited. A second important innovation at this time was the development of single aliquot methods which made it possible to measure equivalent dose (D_E) using a single subsample (called an aliquot) and made it practical to make replicate measurements. Duller et al. (1995) was one of the first to use single aliquot IRSL measurements in glacial environments and analyzed a variety of glacially derived sediments from Scotland. Some of these sites had independent age control, and these showed that while some ages were consistent with the other geochronological methods, others were clearly inconsistent. This was progress over the use of TL methods, but major hurdles still existed. The methods available for analysis of the D_E estimates was crude at that stage, and the measurements of IRSL made at that time were prone to anomalous fading (see “► [Feldspar, Infrared Stimulated Luminescence](#)”).

Development of the single aliquot regenerative dose (SAR) method for OSL measurement of quartz, and improved understanding of the causes of variations in D_E between different aliquots, led to renewed efforts to apply luminescence to glacial sediments. Of particular importance was the development of statistical models such as the minimum age model (see “► [Luminescence Dating, Single Grain Dose Distribution](#)”) which can be used to identify within a set of replicate D_E measurements the population of aliquots which were best bleached at deposition. The development of instruments that were able to make measurements of the OSL signal from single grains (see “► [Luminescence Dating](#)”) was also important for some studies as changing the number of grains in an aliquot can be valuable in ensuring that the best bleached grains are seen (Olley et al. 1999). However, there is still debate within the academic community about whether measurements of single grains are more appropriate than using “small aliquots” where perhaps 10–30 grains are placed on each aliquot (Duller 2008). A common challenge when looking at the OSL signal from quartz isolated from glacial sediments is the low signal intensity, and this can make single grain measurements difficult.

The application of luminescence dating to glacial sediments can usefully be divided into those applications that have studied mountain glaciers and those that have studied sediments derived from large continental-scale ice sheets associated with Pleistocene expansions of ice cover.

Sediments from Mountain Glaciers

In the context of luminescence dating, the critical aspects of glaciers in mountainous terrains are that the transport distance between erosion and deposition of sedimentary material tends to be short, and the source geology is often dominated by intrusive igneous rocks. The impact of these characteristics is to give quartz whose OSL sensitivity is commonly very low. This means that the OSL signal emitted per unit of radiation (Gy) tends to be low and is often near the detection limit of available instruments. This has been a major challenge in areas as diverse as the Himalaya, Scotland, Chile, the Alps in Europe, and the Southern Alps in New Zealand (Preusser et al. 2006). Pietsch et al. (2008) measured the OSL sensitivity of quartz along a river course and showed that it increased downstream, presumably due to repeated cycles of erosion and burial. Such repeated transport cycles are unlikely in mountain glaciers.

These characteristics obviously do not apply to all mountain glaciers, but they are commonly observed. In some studies the quartz has had such low OSL sensitivity that it has not been possible to obtain ages (e.g., Lukas et al. 2007). In other areas it has been possible to obtain ages that are both geomorphologically consistent and which agree with Cosmogenic Nuclide Dating (Glasser et al. 2006). Many studies make measurements of aliquots containing many grains because of the low OSL sensitivity (e.g., Spencer and Owen 2004). Single grain measurements may be possible, though only a very limited proportion of grains may give sufficient OSL signal to be useful (~0.5 % of the grains in the samples from Chile studied by Duller (2006)).

Sediments from Continental-Scale Ice Sheets

In contrast to mountain glaciers, large continental-scale ice sheets typically have greater opportunities to incorporate material from a variety of geological sources, and detrital materials travel longer distances. The spatial scale of the sedimentary deposits also tends to be greater, and this may provide more opportunities for exposure to daylight. This is especially likely for glaciofluvial sediments and glaciolacustrine sediments. One of the largest bodies of work undertaken using luminescence dating was for the QUEEN project (Quaternary Environment of the Eurasian North; 1996–2002), where over 600 OSL ages were measured on quartz extracted from a wide range of sediments associated with former glaciation of the Russian arctic (Svendsen et al. 2004). Measurements on these samples generally showed that the OSL signal from quartz had been effectively reset at deposition (Thomas et al. 2006) presumably because of the long transport distances in such a large ice sheet. Furthermore, low OSL sensitivity is not reported to be a problem in this extensive study.

Conclusions

Luminescence dating of sediments associated with glacial activity is possible, provided that care is taken when sampling to choose facies with the greatest likelihood of exposure to daylight. Luminescence is often the only geochronological method that can be applied to glacial sediments. The

quartz OSL signal is generally the most appropriate signal for dating because it is reset by exposure to daylight so rapidly. However, in some areas the quartz OSL signal is very dim; this may be a challenge, and in extreme cases it may make it impossible to obtain an age. Replicate measurements of D_E , whether on small aliquots or single grains, are essential when studying glacially derived sediments because it provides a means of assessing whether the luminescence signal from the sample was effectively set to zero at deposition or not. Where there is evidence that not all the grains in a sample were reset at deposition, statistical methods such as the minimum age model (see “► [Luminescence Dating, Single Grain Dose Distribution](#)”) may be used to identify the population of grains that were bleached and hence enable accurate dating.

Cross-References

- [Feldspar, Infrared Stimulated Luminescence](#)
- [Luminescence Dating](#)
- [Luminescence Dating, History](#)
- [Luminescence Dating, Single Grain Dose Distribution](#)
- [Terrestrial Cosmogenic Nuclide Dating](#)

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Bomb Carbon

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Synonyms

Bomb ^{14}C ; Bomb radiocarbon; Excess anthropogenic radiocarbon; Excess radiocarbon

Definition

Bomb carbon refers to anthropogenic radiocarbon produced and released into the atmosphere during aboveground nuclear weapons testing, primarily between 1945 and 1963.

Introduction

When Willard Libby introduced the radiocarbon method (Libby et al. 1949), global atmospheric radiocarbon (^{14}C) from nuclear weapons fallout was undetectable. This soon changed, however, as weapons testing programs accelerated during the 1950s and into the 1960s. At the same time, new radiocarbon laboratories were being established in Europe, North America, Africa, and Australia. It did not take long for researchers to discover a dramatic increase in atmospheric ^{14}C from nuclear weapons testing fallout, in both the Northern Hemisphere (de Vries 1958; Broecker and Walton 1959; Münnich and Vogel 1958) and the Southern Hemisphere (Rafter and Fergusson 1957; Münnich and Vogel 1958; Broecker and Walton 1959). This nuclear weapons-related radiocarbon became known as *bomb carbon*. The production of bomb carbon accelerated in the late 1950s and early 1960s as tests became more numerous and the explosive power of nuclear weapons increased dramatically. By 1963, the radiocarbon content of the atmosphere reached its peak when a nuclear test ban treaty put an end to aboveground nuclear weapons testing.

Plotted versus time, atmospheric bomb carbon follows a curve with a sharp increase in the 1950s and with a peak production in the early 1960s. Atmospheric bomb carbon peaks around 1964 and then declines rapidly (Fig. 1). This feature is often referred to as the radiocarbon *bomb pulse*, *bomb spike*, or *bomb curve*. The decline of atmospheric bomb carbon marks the end of aboveground nuclear weapons testing and illustrates the subsequent rapid removal of atmospheric $^{14}\text{CO}_2$ by the oceans (Craig 1957; Revelle and Suess 1957) and biosphere. The oceanic uptake of bomb carbon has been extensively documented by direct seawater analyses (Stuiver et al. 1981; Key et al. 2004), and biospheric uptake is reflected in tree-ring ^{14}C records. These examples represent two primary pathways of the carbon cycle – a global dynamic system that moves carbon within and between the atmosphere, oceans, biosphere, and lithosphere. They also illustrate the chief importance of bomb carbon to science, as an isotopic tracer and time marker.

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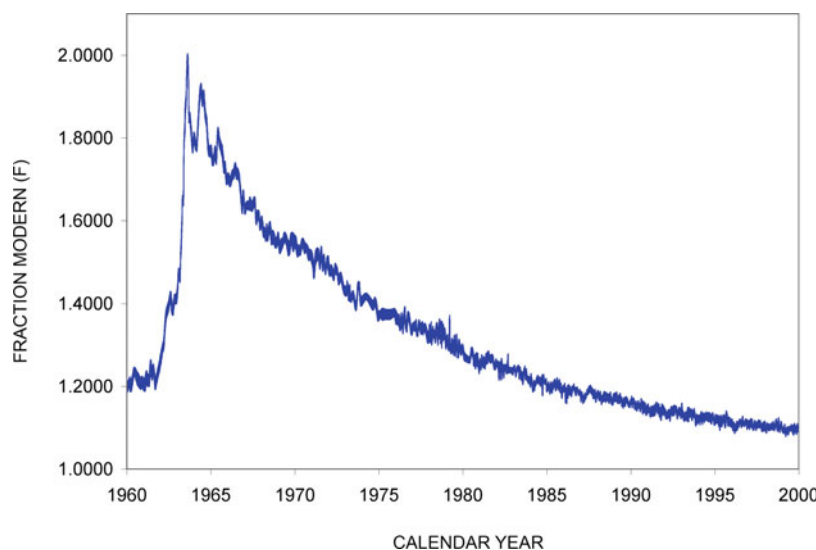


Fig. 1 The radiocarbon bomb pulse. Atmospheric $^{14}\text{CO}_2$ values from northern Europe, expressed as fraction modern carbon (F) values (see text for details) (Data from Levin and Kromer (2004))

^{14}C Production

Radiocarbon is produced naturally in the Earth's atmosphere, as cosmic rays collide with atmospheric molecules. These collisions result in a variety of particles, including secondary thermal neutrons. A portion of these thermal neutrons (n) interact with atmospheric ^{14}N and produce ^{14}C and protons (p) by the reaction:



This is the dominant pathway for the formation of natural radiocarbon on Earth (Libby 1955), and it is a consequence of the relatively large thermal neutron cross section (~ 1.8 barns) for the $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$ reaction (Lal and Peters 1967). Aboveground nuclear weapons tests produce carbon in the same manner as cosmic rays because the atmosphere is rich in nitrogen and both fission- and fusion-based nuclear weapons provide an ample supply of thermal neutrons.

Estimates for the total amount of bomb carbon produced during the years of aboveground nuclear weapons testing are on the order of 10^{28} atoms. These values are usually expressed in multiples of 10^{26} ^{14}C atoms, or in kmol ^{14}C ($1 \text{ kmol } ^{14}\text{C} = 6.02 \times 10^{26}$ atoms). Since atmospheric carbon rapidly exchanges with carbon in the ocean and biosphere, it is not possible to directly measure the integral total production of bomb radiocarbon during the years of testing. An alternative is to estimate a value that sums the output from individual weapons tests. Naegler and Levin (2006) used this approach to estimate total production from 1945 to 1980 at $598\text{--}632 \times 10^{26}$ ^{14}C atoms, based in part on estimates from Enting (1982), Enting and Pearman (1982), Rath (1988), Hesshaimer et al. (1994), Lassey et al. (1996), and Yang et al. (2000). The amount of bomb carbon produced by a particular nuclear explosion is related to the amount of energy released. The precise yield, however, depends on factors such as the type and design of a given nuclear weapon, the altitude of the blast, and environmental conditions (Glasstone and Dolan 1977). These factors lead to intrinsic uncertainties in the calculation of the exact amount of total bomb carbon produced by weapons testing (Tans 1981; Naegler and Levin 2006), hence the broad range quoted above.

The natural production rate of ^{14}C in the atmosphere is currently about $2 \text{ atoms cm}^{-2} \text{ s}^{-1}$ (Castagnoli and Lal 1980). Multiplying this by the surface area of the Earth ($5.1 \times 10^{18} \text{ cm}^2$) and multiplying by 1 year ($3.15 \times 10^7 \text{ s}$) gives a ballpark average for the annual production of natural radiocarbon on Earth, which is 3.21×10^{26} atoms. A comparison with the estimate from Naegler and Levin (2006) implies that the total production of bomb carbon amounts to approximately 190 years of natural production.

Records of Atmospheric Bomb Carbon

Atmospheric records of bomb carbon are important to climate modelers because the bulk of ^{14}C produced by nuclear weapons was injected into the stratosphere. Stratospheric measurements of bomb carbon using aircraft and balloons have been compiled by Telegadas (1971). These data provide constraints on the total bomb carbon production estimates described above (Tans 1981; Naegler and Levin 2006). For the purpose of radiocarbon dating, it is the tropospheric radiocarbon values that are pertinent because the troposphere is in direct contact with the planetary boundary layer where plants and animals live.

Tropospheric records of bomb carbon are obtained from direct measurements of atmospheric CO_2 and from measurements of trees. Trees can be used to reconstruct radiocarbon time series because they incorporate carbon directly from the atmosphere (through photosynthesis) and because they form annual growth rings suitable for age control. Tans (1981) compiled a composite record of global atmospheric and marine bomb carbon using a variety of sources as a database for modelers. Levin and Kromer (2004) published a detailed atmospheric bomb carbon record from Europe, for the period 1953–2003, based on measurements of atmospheric CO_2 . Hua and Barbetti (2004) made a detailed comparison of atmospheric records from around the world. Their results showed a large difference between the two hemispheres, with the highest values in the Northern Hemisphere and lowest values in the Southern Hemisphere (Fig. 2). These differences are much greater than the well-

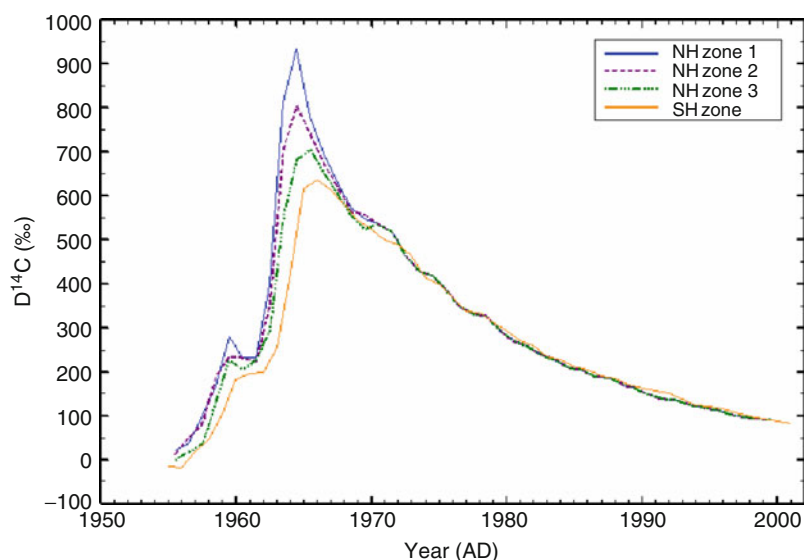


Fig. 2 Atmospheric radiocarbon from nuclear weapons testing in the 1950s and 1960s. Note the different amplitude and rate of increase in the Southern Hemisphere, as compared with the Northern Hemisphere. Zones represented in the figure are *NH1* Northern Hemisphere high-latitude sites, *NH2* and *NH3* Northern Hemisphere mid- to low-latitude sites, and *SH* Southern Hemisphere (Figure from Hua and Barbetti (2004))

known natural differences between the two hemispheres described by McCormac et al. (1998) and Hogg et al. (2002). Hua and Barbetti (2004) also documented bomb carbon zonation within the Northern Hemisphere and proposed four primary curves to describe the bomb pulse: NH1, NH2, NH3, and SH (Fig. 2). As shown below, these records are critical to a bomb carbon age determination because they represent the starting point of a sample for a particular region.

Records of Marine Bomb Carbon

The ocean is the world's largest carbon reservoir (Craig 1957; Revelle and Suess 1957), and characterizing the transfer of bomb carbon into the oceans and its subsequent transport within individual water masses became the subject of intense study following the era of aboveground nuclear weapons testing. The multinational Geochemical Ocean Sections Study (GEOSECS) formally began in 1967 and included a large number of scientific cruises across the Pacific and Atlantic Oceans (Craig 1972, 1974; Craig and Turekian 1976, 1980). A key element of the GEOSECS program was to study the distribution of ^{14}C in marine surface waters and at depth (Stuiver et al. 1981). A second such program, the World Ocean Circulation Experiment (WOCE), was conducted in the 1990s (Key et al. 2004). The WOCE program initiated the construction of a dedicated accelerator mass spectrometry (AMS) facility in Woods Hole, MA, which eventually produced over 13,000 radiocarbon measurements from seawater (McNichol et al. 2000). These and other programs were instituted to provide the type of three-dimensional data coverage and measurement precision necessary for climatological modeling. The records produced are also ideal for radiocarbon dating in the ocean.

A second significant source of marine bomb ^{14}C records comes from radiocarbon analyses of corals (Druffel and Linick 1978; Druffel 1981, 1987). Certain reef-building corals produce annual growth rings that allow for the determination of calendrical ages. When paired with radiocarbon measurements, corals offer an excellent archive for the reconstruction of radiocarbon time series, analogous to the terrestrial example of trees. Many thousands of such dates have now been published, and these feature much finer geographic and time resolution than seawater measurements collected during individual cruises.

Dating with Bomb Carbon

Dating with bomb carbon follows the same logic as traditional radiocarbon dating. A date is determined by comparison of the measured ^{14}C content of a sample with calibrated ^{14}C time series records. The sharp rise and fall of the bomb pulse makes it possible to date very accurately (within a few years) events which occurred since the late 1950s. The ^{14}C content of a sample can be measured using decay counting or by AMS. AMS results are usually expressed as fraction of modern carbon (F) values, defined as (Donahue et al. 1990)

$$F \equiv \frac{\left(^{14}\text{C}/^{13}\text{C} \right)_{\text{sample}[-25]}}{\left(^{14}\text{C}/^{13}\text{C} \right)_{1950[-25]}}, \quad (2)$$

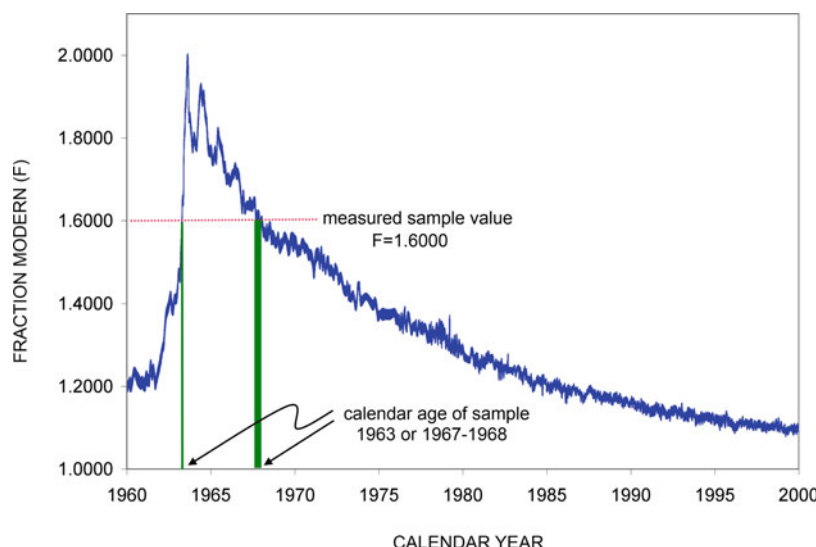


Fig. 3 Sample calculation of a bomb carbon date. The fraction modern carbon value ($F = 1.6000$) is projected onto the atmospheric $^{14}\text{CO}_2$ data of Levin and Kromer (2004) along the dashed line. This gives two possible ages for the sample, at 1963 and 1967–1968. The width of the atmospheric curve includes two sigma uncertainties

where $(^{14}\text{C}/^{13}\text{C})_{\text{sample } [-25]}$ is the measured ratio of the sample, corrected to $\delta^{13}\text{C} = -25\text{‰}$, and $(^{14}\text{C}/^{13}\text{C})_{1950 [-25]}$ is the $\delta^{13}\text{C}$ -corrected ratio for the standard, adjusted for decay to the year 1950 (the “zero” year for radiocarbon dating).

Figure 3 shows an example of a radiocarbon age determination using bomb carbon for a sample with a fraction modern carbon value of $F = 1.6000 \pm 0.0050$. This example employs the atmospheric curve of Levin and Kromer (2004), appropriate for northern Europe. The age of the sample is determined by projecting the measured F value onto the bomb carbon curve. This gives two possible ages: (1) in 1963 and (2) 1967/1968. The uncertainties in this procedure can be obtained graphically or calculated. The CALIBOMB program, supported by Queen’s University Belfast, is freely available to calculate and plot bomb radiocarbon dating results using the Levin and Kromer (2004) dataset (www.calib.org).

Applications of Bomb Pulse Radiocarbon Dating

The application of bomb pulse radiocarbon dating cuts across many disciplines. The common feature of these studies is that they are concerned with events that transpired within the past 50 years. Recent examples from the literature include the following: (1) Fisheries Sciences, where bomb carbon dating has been used to determine the age of fishes as a critical component of population assessments (Andrews et al. 2011; Passerotti et al. 2010); (2) Forensic Sciences, where bomb carbon dating has assisted in the identification of crime victims (Speller et al. 2012) and to analyze the production to marketing cycle of the illicit drug trade (Ehleringer et al. 2012); (3) Earth Sciences, where bomb carbon has been used to determine the growth rate of cacti in reconstructing records of precipitation (English et al. 2010) and to determine the growth rate of speleothems (Hodge et al. 2011); and (4) Environmental Sciences, where bomb carbon has been used to determine rates of recent soil development and shoreline accretion (Lovelock et al. 2010). Applications of bomb pulse radiocarbon dating have expanded in recent years, and with radiocarbon’s

relatively long half-life ($\sim 5,700$ years), it is likely that this expansion will continue into the foreseeable future.

Summary

Aboveground nuclear weapons testing conducted between 1945 and 1963 nearly doubled the amount of ^{14}C in the atmosphere with the addition of bomb carbon. After the nuclear test ban treaty was signed in 1963, this excess atmospheric radiocarbon rapidly diminished through exchange with the oceans and biosphere. This rise and fall of atmospheric radiocarbon created a global radiocarbon bomb pulse that serves as a time marker for a wide range of dating applications.

Cross-References

- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Otolith](#)

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Electron Spin Resonance (ESR) Dating of Coral

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Synonyms

Electron paramagnetic resonance (EPR) dating

Definition

Electron spin resonance (ESR) dating. Radiation exposure dating method using radiation-sensitive ESR signals, which operate like natural dosimeters. An ESR age calculation derives from the ratio of the accumulated dose (DE) of a sample to the background natural radioactivity within a range of 30 cm and cosmic doses.

Introduction

Electron spin resonance (ESR; sometimes called electron paramagnetic resonance, EPR) dating of corals has become an efficient tool in earth sciences for paleoenvironmental studies on coral reef terraces in the last 20 years. The first systematic studies and geochronological applications of ESR dating of corals started in the 1980s and early 1990s. They were carried out on sites with raised coral reef tracts in southern Japan (e.g., Ikeya and Ohmura 1983; Ikeya 1983), in Haiti (Skinner 1985), and in Barbados (Radtke and Grün 1988; Radtke et al. 1988; Grün et al. 1992). Since then, several methodological improvements and the development of more stable and high-resolution ESR spectrometers have significantly increased the quality of ESR dating results. The latter is strongly supported by the comparison of ESR dating results with radiocarbon (^{14}C) and TIMS $^{230}\text{Th}/^{234}\text{U}$ data (see below). By ESR dating of raised coral reef terraces, it is possible to distinguish between the major periods of high sea level during the last 500,000 years but also to differentiate between submaxima, for example, the submaxima MIS 5a-1 (c. 74 ka), MIS 5a-2 (c. 85 ka), MIS 5c (c. 105 ka), MIS 5e-1 (c. 118 ka), and MIS 5e-2,3 (ca. 128–132 ka), during the MIS 5 sea-level highstand (e.g., Schellmann et al. 2004; Schellmann and Radtke 2004a). However, an accurate differentiation between MIS 9, MIS 11, and older sea-level maxima is often limited by considerable alterations and recrystallization processes within these older coral samples. Also, the problem of natural “ESR rejuvenation,” which is the recombination of electrons that increases until a natural equilibrium is reached, must be addressed (e.g., Grün 1989; Rink 1997; Jonas 1997).

Physically, the upper dating limit of the ESR method is defined by this natural equilibrium limit. Despite this, weak weathering and slight recrystallization from a primary aragonite to a calcite

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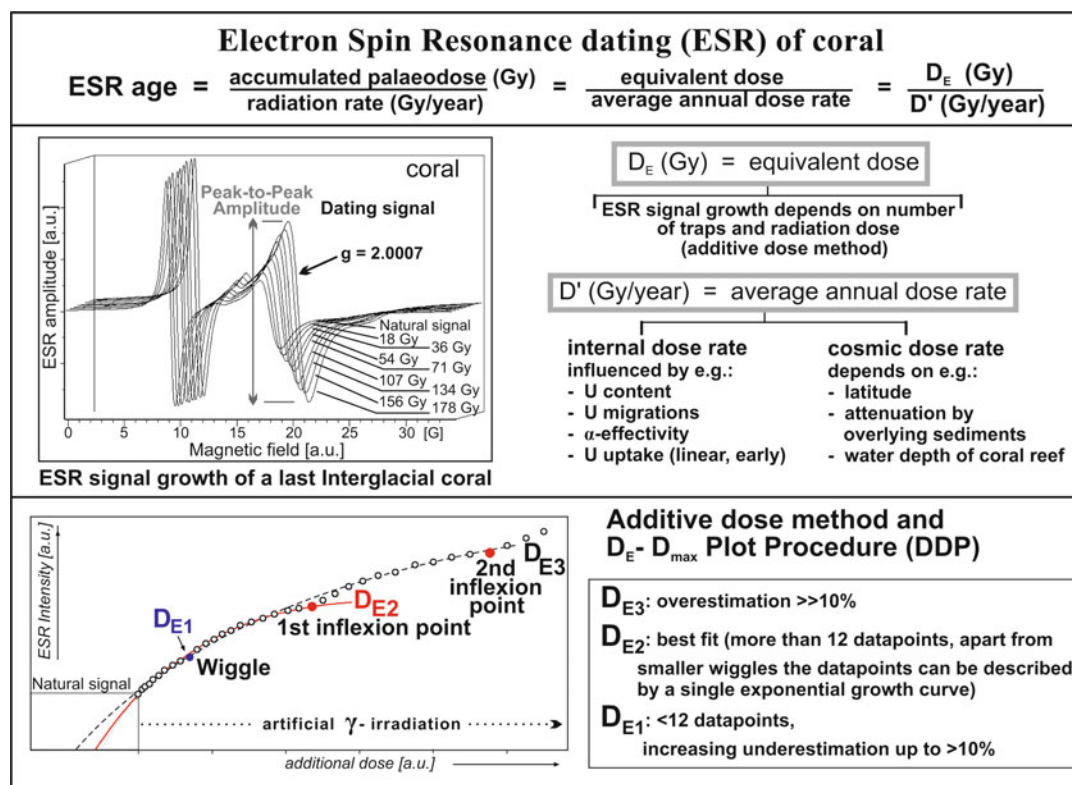


Fig. 1 Generalized principle of ESR dating of aragonitic coral.

coral fabric, which defines age rejuvenation effects, often cause a progressive underestimation of ESR ages before this upper dating limit is reached.

Methodology

The electron spin resonance (ESR) dating technique is one of several radiation exposure dating methods based on radiation dosimetry such as thermoluminescence (TL), optically stimulated luminescence (OSL), and radioluminescence (RL). All these methods use the phenomenon of common minerals, like the aragonite fabric of corals, acting as natural dosimeters. The radiation (natural radioactivity and cosmic rays) causes charges (electrons, free radicals) which are trapped at defects in the crystal lattice of a wide range of minerals. This naturally accumulated dose can be determined by ESR. The basic principles of the physics and the application of the ESR dating technique have been provided, for example, by Walther et al. (1992), Ikeya (1993), Rink (1997), Jonas (1997), Sharaf and Hassan (2004), Blackwell (2006), and Grün (2007). Schellmann et al. (2008) have reviewed the accuracy of ESR dating of corals, mollusk shells, and quartz. Blackwell et al. (2007) used coupled $^{230}\text{Th}/^{234}\text{U}$ and ESR coral dating for reconstructing sea-level changes since the last interglacial maximum (MIS 5e).

Here, we will focus on ESR dating aragonite coral samples. The time-dependent accumulations of trapped charges form paramagnetic centers, which can be detected by the rise of the ESR signal at $g = 2.0007$ (Fig. 1). Multiple scans (e.g., 5–40 scans) increase the precision of ESR signal amplitude measurements. The amount of trapped charge accumulation (paleodose, D_E) increases with time and can be quantified by ESR.

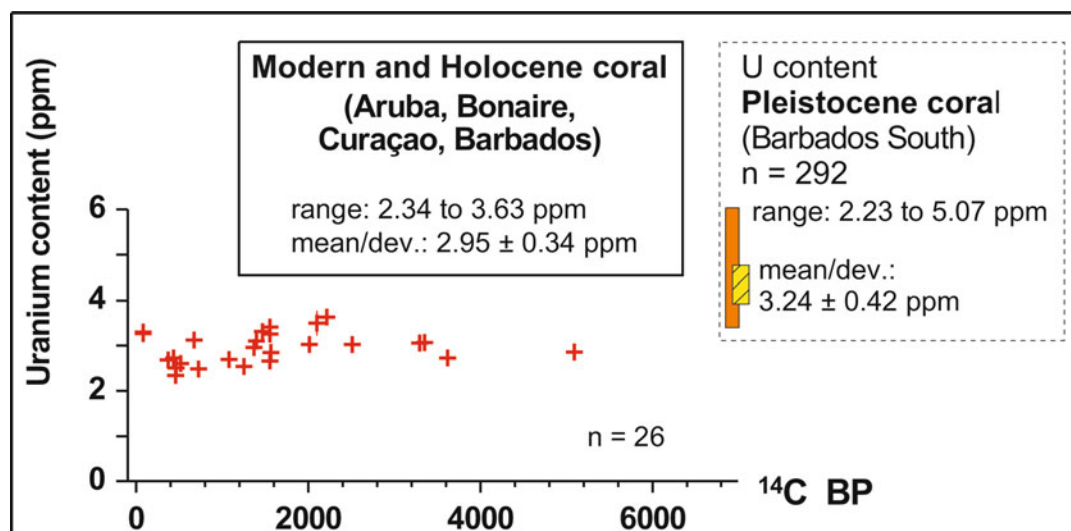


Fig. 2 Uranium content (ppm) of modern, Holocene, and Pleistocene corals (Details are provided in Schellmann et al. (2008)).

An ESR age is derived from the ratio of the accumulated radiation dose D_E (equivalent dose) to the natural radiation rate D' (dose rate) within a range of 30 cm, to which the sample was exposed in the past (Fig. 1). The D_E is determined by an additive dose method. For this method, more than 12 aliquots (Schellmann and Radtke 2001) of the same sample are stepwise irradiated with increasing artificial γ -doses (e.g., using a ^{60}Co gamma source). The growing amplitude of the ESR signal at $g = 2.0007$ of a coral sample is proportional to the number of trapped charges (D_E), which is dependent on the strength of natural irradiation (dose rate, D') and on the radiation time (=age of the sample). A living coral does not contain the ESR dating signal at $g = 2.0007$, which means the ESR intensity is zero. The D_E is determined by extrapolating the resulting dose-response curve to zero ESR intensity. In the case of dating corals or mollusk shells, the D_E – $D_{\max}$ plot procedure (D – DP procedure) should be used for the calculation of D_E (Fig. 1) as described by Schellmann and Radtke (2001).

The former natural dose rate (D') of a coral sample is estimated based on the content of uranium (U) (other radioactive elements like thorium and potassium are of no relevance) and the intensity of the cosmic dose rate (Prescott and Hutton 1994). Most colonial corals of sub-modern, Holocene, and Pleistocene corals have mean U contents of about 2.9–3.2 ppm (Fig. 2). This illustrates a prevailing U uptake of corals from seawater during their lifetime or shortly after death. Consequently, ESR ages of corals should be calculated using a recent or early U uptake model. However, some extremely high (up to 5 ppm) and low (below 2.5 ppm) U concentrations indicate significant U loss or gain; both limit a reliable age determination. But U-series dating results of corals are strongly influenced by U migrations than ESR. Therefore, the application of both methods can be valuable. For dose rate calculation, an alpha efficiency (k-factor) of 0.06 ± 0.02 should be used (Grün 2007). The correct determination of D' and D_E is essential for any ESR age estimation. The average error range when dating corals is between 5 % and 8 %.

Improvements in annual dose rate (D') estimation and the newly developed approach of equivalent dose (D_E) determination (D_E – $D_{\max}$ plot procedure) increase the precision of ESR dating Holocene and Pleistocene corals (Schellmann et al. 2008). This is strongly supported by comparing ESR dating results with other numeric dating methods such as radiocarbon (^{14}C) and TIMS U-series analysis (TIMS $^{230}\text{Th}/^{234}\text{U}$). Such correlations are published, e.g., by Radtke et al. (2003),

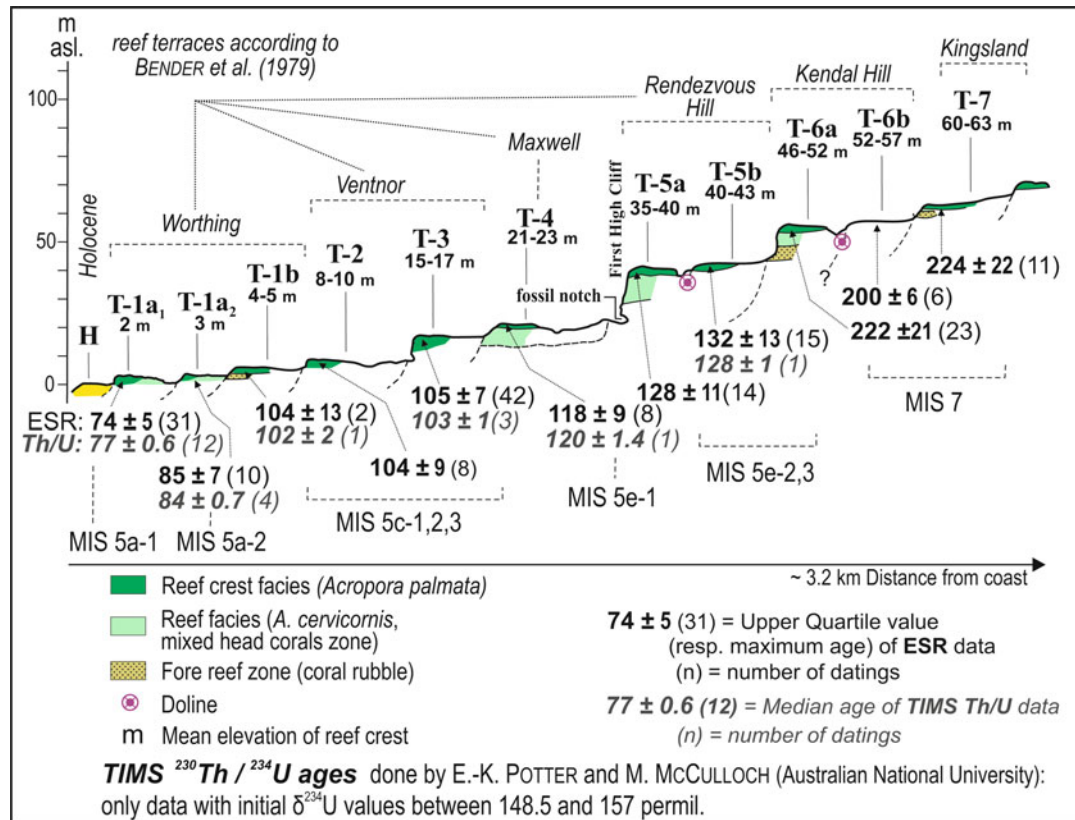


Fig. 3 ESR and TIMS Th/U ages of uplifted Middle and Late Pleistocene coral reef terraces in a transect on southern Barbados (Details are provided in Schellmann and Radtke (2004a, b)).

Schellmann et al. (2004, 2008), and Muhs et al. (2012). They are exemplarily illustrated in the following case study from Barbados.

Case Study: ESR Dating of Pleistocene Coral Reef Terraces

The elevated coral reef terraces on the Caribbean island of Barbados are a typical region for both the reconstruction of Late and Middle Pleistocene sea-level changes (classical “Barbados Model”) and, as one of the most common applications of ESR dating, the accuracy of ESR dating results on fossil corals up to c. 600 ka. Since early systematic studies by Radtke et al. (1988) and Radtke (1989), new geological, morphostratigraphic, and chronostratigraphic investigations during the past two decades led to several methodological improvements of ESR dating on coral and deliver some impressive examples of the application of this method (e.g., Schellmann and Radtke 2004a, b).

On southern Barbados, several uplifted Pleistocene coral reef terraces formed during oscillating MIS 5 and MIS 7 sea-level maxima are well preserved between the present coastline and the inland (Fig. 3). They rise up to 67 m above modern sea level (asl) and are accompanied to the center of southern Barbados by more elevated older Middle Pleistocene coral reefs formed during MIS 9 to MIS 11 sea-level highstands. Based on geological, morphostratigraphic, and chronostratigraphic methods, the uplifted MIS 5 and MIS 7 coral reefs of southern Barbados can be subdivided into up to seven clearly distinguishable main coral reef terraces (T1 to T7) and some less prominent

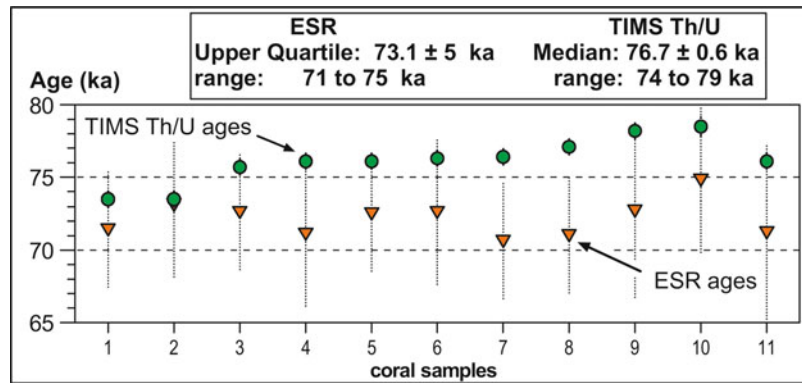


Fig. 4 ESR and TIMS Th/U ages ($\delta^{234}\text{U} > 141$ and $< 157\text{‰}$) of MIS 5a-1 coral reef terrace near Inch Marlowe Point, southern coast of Barbados (Modified after Schellmann and Radtke (2004a), and Schellmann et al. (2004)).

sublevels (e.g., T-6a and T-6b, T-1a₁ and T-1a₂). The youngest reef terraces are located at the lowest elevations close to the present coast, while older reef tracts have higher elevations and generally a greater distance from the coast. Due to the relatively slow uplift rate in southern Barbados (approx. 0.27 ± 0.02 m/1,000 a), the youngest Late Pleistocene coral reefs (T-1a₁) have been formed during MIS 5a-1 at approx. 74 ka (ESR) or 77 ka (TIMS Th/U) and the oldest and highest MIS 7 reef terrace (T-7) during a MIS 7 sea-level maximum approx. 224 ka (ESR). Both dating methods support in general a geochronological differentiation of the MIS 5a reefs into two sea-level submaxima (T-1a₁, T-1a₂) around 74 ka (ESR) or 77 ka (Th/U), and 85 ka (ESR) or 84 ka (Th/U). The three T1b, T2, and T3 coral reef terraces were formed during the MIS 5c around 104–105 ka (ESR) or 102–103 ka (Th/U). The three coral reef terraces (T4, T5a, T5b) are of MIS 5e age around c. 118 ka (ESR) or 120 ka (Th/U), and 132 ka (ESR) or 128 ka (Th/U) for the oldest MIS 5e reef terrace, respectively. However, an age differentiation of the three MIS 7 reef terraces (T6a, T6b, T7), which were formed around 200–224 ka (ESR), is still not possible. The correlation between age and height of the reef terraces allows to calculate neotectonic movements and to estimate paleo-sea-level changes (e.g., Schellmann et al. 2004; Radtke and Schellmann 2005).

The example shows that generally the timing of coral reef growth determined by both dating methods agrees well, especially when the error ranges are considered. However, ESR and TIMS Th/U age estimates from an MIS 5a-1 coral reef near the south point of Barbados (Fig. 4) illustrate that many ESR ages are up to 5–10 % younger than the corresponding U-series dates, respectively. The U-series data shows a slightly overestimation of the expected age. This data set illustrates very well that the apparently minor analytical errors (precision) of U-series data (less than 1 %, ESR between 5 % and 8 %) give no evidence of a better time resolution (Schellmann et al. 2004). The age estimates were carried out on paired samples. They show that the spread of individual ages (not considering errors) for both methods is about 4,000 year, although all ages were produced on individuals from the same branch of coral, which are hence most likely of the same age (grown within not more than a few hundred years). Therefore, age differentiations between single Late Pleistocene coral reef deposits that have developed in time periods of less than 4,000–5,000 years are little reliable, independent from the applied dating technique (ESR or TIMS U-series).

Summary and Conclusions

Due to methodological advances, which significantly increase the accuracy of ESR dating of Pleistocene and Holocene corals, ESR dating has become an efficient tool in earth sciences in the past two decades, especially for geochronological studies on coral reef terraces. ESR dating of Pleistocene corals permits to differentiate between the main Marine Isotope Stages (MIS) 5, 7, 9, 11, and 13 as well as between the substages 5e-2,3 and 5e-1, 5c, and 5a-2 and 5a-1. The average error is about 5–8 %. Late Pleistocene corals can be dated with a similar accuracy as with the TIMS U-series method in this time range, although the individual errors of ages are significantly larger than those of U-series data. The advantage of ESR, however, is that the upper dating limit for corals is probably above 500,000 year. If weathering and recrystallization from primary aragonite to calcite of the coral material could be excluded, dating of coral with an age of several million years should be feasible from the physical point of view. All in all, future research in ESR dating corals should be focused on the creation of a single-aliquot dating technique, which uses orientated aragonitic polycrystals.

Cross-References

- ▶ [Electron Spin Resonance Dating](#)
- ▶ [Electron Spin Resonance Spectrometer](#)
- ▶ [Geological Time Scale](#)
- ▶ [Marine Isotope Stratigraphy](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Radiation Defect](#)
- ▶ [Radiation Dose Rate](#)
- ▶ [Relative Dating Methods](#)
- ▶ [Uranium Series Dating](#)
- ▶ [Uranium Series, Marine Carbonates](#)
- ▶ [Uranium-Thorium-Helium Dating](#)

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Walther's Law of Facies

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Synonyms

Walther's law; Law of facies

Definition

The Walther's Law of Facies was introduced by the German geologist Johannes Walther (1860–1937) as an important geological principle, after the establishment of the concept of “facies,” one of the foundations of modern stratigraphy. Walther's Law states that any vertical progression of facies is the result of a succession of depositional environments that are laterally juxtaposed to each other.

The original definition (Walther 1894) reads as follows and was translated from the original German language by G. Middleton in 1973:

The various deposits of the same facies-area and similarly the sum of the rocks of different facies-areas are formed beside each other in space, though in a cross section we see them lying on top of each other. As with biotypes, it is a basic statement of far reaching significance that only those facies and facies-areas can be superimposed primarily which can be observed beside each other at the present time.

– Walther's Law of Correlation of Facies (1894)

Contextual Background

A “sedimentary facies” or simply “facies” is a term assigned to a sedimentary rock unit referring to its distinct and specific identifiable (i.e., descriptive) characteristics, produced by physical, biological, and/or chemical processes, during formation and from which an interpretation of its origin may be made (Middleton 1973; Reading 1996). Hence, a facies is generated during specific sedimentological conditions, reflecting a distinct depositional environment and associated processes. They can be single layers (few millimeters thick) or a series of thick beds (tens to hundreds of meters thick).

Sedimentary facies can be grouped spatially by associating genetically related lithologies that reflect linked environments in the stratigraphic record. This is known as a lateral association or assemblage of sedimentary facies (also called a facies tract) and is usually a lithofacies (rather than biofacies). Another type of association is the “facies sequence” which is a term assigned to distinct vertical stacking, succession, or sequence of facies that reflects a particular depositional environment or linked environments in the stratigraphic record (Middleton 1973).

Walther's Law simply states that both vertical and lateral facies match. A depositional system may contain several environments. Deltas contain channels, mouth bars, and prodelta muds, and consequently the sedimentary rock types (i.e., facies) in a depositional system may be variable, recording

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the specific characteristics of their component depositional conditions (e.g., sandy channels and mouth bars, muddy prodeltas). However, these environments can shift laterally causing sediment to stack vertically. As a depositional environment shifts, so too must the sedimentary facies in any one location change. As time progresses, the positions of facies also progress laterally in space and time; hence, the laterally related environments become superimposed forming vertical successions. This process results in deposition of time-transgressive sedimentary formations, in which the vertical stacking of facies records the originally laterally continuous environments (Reading 1996; Middleton 1973). Sedimentary environments that were once laying down side-by-side (facies tracts) will eventually end up overlapping one another over time, forming vertical facies successions, reflecting successive changes in the environment such as marine transgressions and regressions.

Facies associations (vertical and lateral) allow the study of sedimentary facies in space and time and their relationship with longer-term cycles, such as relative sea-level changes or tectonic phases, and subsequent accumulation in sedimentary basins (Friedman et al. 1992). The combination of both lateral facies tracts and vertical facies successions can be used to map broader three-dimensional depositional systems tracts that migrate through time and space as a function of cyclic forcing, such as eustasy. Identifying and mapping these depositional systems tracts and how they change through time are a fundamental component of Sequence Stratigraphy and an important strategy in the interpretation of the origin of sedimentary rocks and paleogeographic reconstructions (Friedman et al. 1992).

Geography, eustasy, isostasy, tectonism, and sediment supply are major controls on the relationships between stratigraphic facies. A classic example of the Law of Facies is the vertical stratigraphic sequence depicting marine transgressions and regressions.

Walther's Law of Facies is applicable only when the sedimentary sequence is continuous, with no hiatuses or breaks.

Cross-References

► [Biostratigraphy](#)

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Dendrochronology, Progress

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Definition

Dendrochronology derives from the Greek words “dendron” (tree) and “chronology” (study of time), and it allows for the precise dating of annual tree rings based on the analysis of tree-ring patterns among several trees. Dendrochronology combined with other disciplines has allowed for substantial progress in environmental studies (see [Cross-References](#)).

Introduction

During recent years, dendrochronologists have faced the challenge of getting more information from tree rings, pushing its own limits to understand a wider range of climatic/environmental factors, to obtain seasonal resolution, and to reconstruct larger spatial scales and longer temporal time spans of climate variability. This is important because instrumental records cover only a limited time period and are insufficient for characterizing decadal and centennial climatic features. Different strategies are being explored to address these challenges. First, different standardization approaches have been designed to retain lower frequencies of climate variability, a frequent pitfall of traditional standardization methods used in tree-ring research. Low and medium frequencies allow us to assess long-term variations in climate and to determine the magnitude and range of climatic conditions through time. This information provides a context to investigate, for instance, whether the recent anthropogenic upward temperature trend is unusual compared to other persistent warm periods during the past, such as one occurring during Medieval Times. Second, several technological advances have allowed for measuring other tree-ring parameters in addition to the more classical methods (i.e., the width and the maximum density of the rings). Stable isotope analyses that include geochemistry and mass spectrometry, as well as wood anatomy analyses using high-resolution imaging, are becoming some of the most popular approaches in the search for different kinds of environmental information. These and other related topics are discussed in the sections below.

Standardization Methods

Tree-ring width series often consist of different components, such as age-size growth trends, environmental signals (e.g., climate variability), growth patterns due to disturbance, and noise. The objective of the study defines which component is considered signal or noise. Therefore, retaining the signal of interest (or removing the noise) in the tree-ring data determines the standardization

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method to be chosen. **Standardization** is the process through which we convert individual tree-ring measurements into dimensionless indices to create a site chronology. This step is used to first make all the trees equally contribute to the mean of the site chronology and second to reduce or remove variability in tree-ring series that is not of interest for the overall research question. For instance, the removal of any nonclimatic variability in tree-ring measurements (e.g., age-size trend) is necessary to retain as much climatic information as possible, and it is one of the greatest challenges in dendroclimatology. Proper removal of nonclimatic trends might suggest that the resulting indices represent an ideally pure climatic signal. The concept of standardization is fairly simple in theory, but the practice has proven to be much more complex. Some new methods designed to preserve as much climatic information as possible are discussed in the following.

The traditional methods of standardization have been outlined and thoroughly discussed in several publications (e.g., Fritts 1976; Cook and Kairiukstis 1990). Perhaps the most basic of these methods is removal of the age-size growth trend through fitting deterministic sloping lines or negative exponential curves to the measurement series (Fritts 1976). However, several adaptations and improvements to this method have been applied within the last few decades, such as standardization methods for closed-canopy forests or trees with potential disturbance signals using stochastic (i.e., flexible) curves such as the cubic smoothing spline (Cook and Peters 1997; Cook 1985). Additionally, attempts have been made to reduce variance biases from the conventional “ratio” method of calculating tree-ring indices through the “residuals” method in conjunction with power transformation (Cook and Peters 1997; Helama et al. 2004). Please refer to an earlier version of the encyclopedia for more specific information on the classical standardization techniques (Buckley 2009). All standardization methods have their own advantages and disadvantages, and the method(s) used for a particular study must consider the trees and the environment in which they are located. However, as a common feature, all these traditional methods are based on data-adaptive curve-fitting approaches that limit the preservation of medium- and low-frequency variability. The extent of longer-term variability removed depends on the chosen detrending method, though the longest timescales are restricted by the “segment length curse” (Cook et al. 1995) to periods below the age of the trees. Thus, further progress in standardization and chronology building has been towards retaining as much low- and medium-frequency climatic information as possible while mitigating (1) the noise inherent in tree-ring series and (2) biases and trend distortion from statistical procedures. We will elaborate on some of the more recent developments that have been especially important in dendroclimatology: the regional curve standardization (RCS), signal-free standardization methods, and the combined step and trend (CST) intervention approach.

Regional Curve Standardization

Regional curve standardization (RCS) was popularized in dendroclimatology primarily by Briffa et al. (1992), and its primary goal was to recover more low-frequency variability in tree-ring chronologies for understanding changes in climate from a long-term perspective. This method aligns individual series by age and then compares each ring width with a regional curve representing an “expectation of growth” to produce indices. For more specifics on computation, please refer to Briffa and Melvin (2011). The RCS method can recover more low-frequency information than other curve-fitting methods of standardization because indices from the latter are forced to have an equal mean (1995), whereas RCS allows for varying index series means through time (Briffa et al. 1992; Briffa and Melvin 2011). There are several important limitations and potential biases to consider when using RCS to produce a site chronology: the “trend-in-signal,” the “differing-contemporaneous-growth-rate,” and the “modern-sample” bias. Briffa and Melvin (2011) describe these biases in detail. In short, the “trend-in-signal” problem occurs when climate signals nearing or extending beyond the full length of

the chronology remain in the RCS mean, thereby under or (over) estimating the final chronology at the beginning and end. This bias can be reduced, in part, by having many overlapping series. The “modern-sample” bias, which is related to the “contemporaneous-growth-rate” problem, should also be seriously considered before using RCS. This bias occurs as a result of the relationship between growth rate and tree longevity. For example, if the number of fast-growing young trees is proportionally greater than slow-growing old trees in a set of all living trees, there will be a positive trend bias in the final chronology. Despite these biases, this standardization method is very powerful for retaining low-frequency variability beyond other methods if the input tree-ring data is appropriate. The RCS performs the best when there are (1) pith-offset estimates in the case where pith dates are not achieved, (2) a sufficient number of samples (Melvin 2004), and (3) many overlapping series of subfossil wood to account for issues with the “trend-in-signal” and “modern-sample” biases.

Signal-Free Method

The signal-free (SF) method introduced by Melvin (2004) and Melvin and Briffa (2008) seeks to reduce the effect of trend distortion that has been recognized using other standardization methods (both traditional and RCS). Trend distortion occurs when variance in tree-ring measurements related to climate is removed during the process of removing age-size growth trends with data-adaptive curve fitting (Melvin 2004). This method produces a series of signal-free measurements, which are void of the common (climate) signal, and develops detrending curves based on the age-size growth-related trend of the signal-free measurements; these detrending curves are applied to the original measurements, thereby producing new indices, and the entire process is iterated as many times as needed until convergence is attained and a final chronology (with reduced trend distortion) is produced. In the effort to infer past climate while preserving low-frequency variability, recent studies have implemented and adopted the SF method (Anchukaitis et al. 2013) or even combined SF with RCS (Björklund et al. 2012). The signal-free method in conjunction with RCS might retain more low-frequency information while also helping to mitigate some of the potential biases imparted on final chronologies from RCS (Briffa and Melvin 2011).

Combined Step and Trend (CST) Intervention Approach (by Daniel Druckenbrod)

In closed-canopy forests, scientists have long observed that understory trees may experience a rapid increase in growth with removal of the canopy above them (e.g., Marshall 1927). This growth increase is typically referred to as a release from suppression (Oliver and Larson 1996) as the tree experiences greater light availability, which in turn provides greater growth. Light availability constitutes an important nonclimatic forcing of tree growth in these forests and is one example of a larger class of disturbance events (e.g., ice storms, insect defoliations, etc.) included within a common conceptual model of tree growth (Graybill 1982; Cook 1987). Identifying and removing disturbance forcings has been challenging for limiting noise in standardizing tree rings. Time series analysis (Box and Jenkins 1970) provides a statistical framework for quantifying the behavior of systems through time, particularly autocorrelated series like tree rings, and has led to advances in climate reconstruction (e.g., Cook and Kairiukstis 1990; Fritts 1976). Downing and McLaughlin (1990) demonstrated that time series analysis with intervention detection could also be applied to identify disturbance events (i.e., interventions) as step outliers in time series when examining red spruce decline; however, few studies have utilized this approach (see Druckenbrod 2005). Druckenbrod et al. (2013) introduced a new combined step and trend (CST) outlier approach that is capable of identifying disturbance events in time series and removing their impact on the subsequent growth rates of trees. After power transforming, removing the age-size growth trend,

and estimating the autoregressive order of a tree-ring time series, this method iteratively searches for outliers in the means of residuals with a running window specified by the user. Disturbance events causing growth suppressions can also be detected similar to Downing and McLaughlin (1990). While this method is new, it also shows potential for use in standardizing tree rings, possibly along with other methods such as RCS and signal-free, since it shares a common framework in time series analysis.

Pseudoproxy Experiments

Pseudoproxy experiments (e.g., Mann and Rutherford 2002) have been recently conducted by Anchukaitis et al. (2013) to evaluate the appropriateness of a set of detrending approaches to minimize the loss of low-frequency variability and trend distortion in real data when reconstructing the target climatic variable. The first step is the generation of a set of artificial pseudoproxies created by a combination of known pseudoclimate signals and growth curves with random noise. The second step is the standardization of these pseudoproxies with different methods (e.g., data-adaptive curves, RCS, or signal-free). Finally, comparisons between the known pseudoclimate and the pseudoclimate estimated with the pseudoproxies standardized in different ways can be achieved. This method allows for detecting potential artifacts directly derived from the chosen detrending method.

Tree-Ring Parameters

Stable Isotopes

The application of **stable isotopes** in tree-ring research continues to be an emerging field (Gagen et al. 2011), but one with great promise for yielding a better understanding of climatic controls and physiological processes driving growth patterns of forests. Significant relationships between well-replicated, absolute-dated tree-ring isotopic chronologies and environmental variables have been well demonstrated in paleoclimatic research (Robertson et al. 2008). Stable isotopic ratios can potentially record climatic variability at all temporal frequencies, and statistical age/geometry detrending is not required (McCarroll and Loader 2004; Gagen et al. 2007; Young et al. 2011; but see Esper et al. 2010). This is a big advantage considering the issues associated with detrending methods (as described above) for generating tree-ring chronologies based on the classical parameters (ring width and maximum latewood density). Indeed, stable isotopic signatures in tree rings can complement the traditional metrics used in dendroclimatology; they can provide a broader spatial signal, preserve low frequencies of climate variability, and reflect different climatic variables (Gagen et al. 2011) for different seasons. Stable isotopes in tree rings are strongly related to climate and atmospheric dynamics and, thus, are powerful paleoclimatic proxies that in some cases record stronger climatic signals than the classical parameter of ring width (Andreu et al. 2008; Gagen et al. 2011).

R denotes the ratio of the heavier isotope (e.g., ^{13}C) to the lighter (e.g., ^{12}C), and it is expressed in delta (δ) notation in parts per thousand (‰) with reference to a standard material of known isotopic ratio:

$$\delta_{\text{sample}} = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1,000$$

The chosen standard for d_{13}C was a subfossil belemnite from the Pee Dee formation of South Carolina, which was exhausted and replaced by Vienna Pee Dee Belemnite or VPDB (Coplen 1995). The $\delta^{18}\text{O}$ signatures are in relation to the Standard Mean Ocean Water (SMOW), now replaced by Vienna-SMOW or V-SMOW, and less often, the Standard Light Antarctic Precipitation (SLAP) can

also be used (IAEA 1995). The hydrogen isotopes (the lighter ^1H , and the heavier ^2H or D, also called deuterium) are expressed as the D/H ratio (δD) and use the same reference materials as $\delta^{18}\text{O}$ ratios (IAEA 1995). Carbon and oxygen stable isotopes are the most frequently used in tree-ring research, and occasionally hydrogen. Here we primarily discuss carbon, but we direct readers to McCarroll and Loader (2004) for a more extended discussion of oxygen and hydrogen.

Stable carbon isotopes can supply distinct types of physiological information including intrinsic water-use efficiency or intercellular CO_2 concentrations to study physiological responses of trees to environmental changes (e.g., Feng 1998; Saurer et al. 2004; Waterhouse et al. 2004; Peñuelas et al. 2010; Andreu-Hayles et al. 2011). The physiological basis of $\delta^{13}\text{C}$ isotopic signatures in tree rings involves several processes and assumptions. Carbon isotope discrimination against ^{13}C (Δ) is calculated expressing the difference in isotopic composition between air ($\delta^{13}\text{C}_{\text{air}}$) and plant organic matter ($\delta^{13}\text{C}_{\text{tree}}$) in ‰ (Eq. 1). For C3 plants, the relationship between Δ and leaf gas exchange can be described by the Farquhar et al. (1982, 1989) model in Eq. (2).

$$\Delta = \frac{\delta^{13}\text{C}_{\text{air}} - \delta^{13}\text{C}_{\text{tree}}}{1 + \delta^{13}\text{C}_{\text{tree}}/1,000} \quad (1)$$

$$\Delta \approx \delta^{13}\text{C}_{\text{air}} - \delta^{13}\text{C}_{\text{tree}} = a + (b - a) \frac{c_i}{c_a} \quad (2)$$

The terms c_i and c_a are the needle intercellular spaces and ambient concentrations of CO_2 ($\mu\text{mol mol}^{-1}$), respectively. Isotopic fractionation is based on two main steps: diffusion (4.4‰) and carboxylation by the photosynthetic rubisco enzyme (~27‰; Farquhar and Richards 1984). First, air diffuses through stomata into the intercellular air spaces towards the carboxylation sites. The CO_2 with the lighter carbon isotope diffuses more easily. Thus, internal air is depleted in ^{13}C relative to ambient air. Second, CO_2 is used by the rubisco and discrimination against $^{13}\text{CO}_2$ is taking place, since biological processes tend to use ^{12}C in preference to ^{13}C .

Knowing Δ , c_i/c_a , and c_i , the intrinsic water-use efficiency (iWUE) can be estimated. Δ can be calculated using extrapolations of $\delta^{13}\text{C}_{\text{atm}}$ mainly derived from Antarctic ice-core records (Francey et al. 1999) and direct measurements, summarized by McCarroll and Loader (2004). The c_i can be determined using the data of the c_a from Robertson et al. (2001) until 1993 and from Mauna Loa from 1994 to 2007 (composite series published in McCarroll et al. (2009)). The iWUE is the ratio of the fluxes of net photosynthesis A and conductance for water vapor $g_{\text{H}_2\text{O}}$ (Ehleringer et al. 1993; Feng 1999):

$$\text{iWUE} = \frac{A}{g_{\text{H}_2\text{O}}} = (c_a - c_i) \frac{1}{1.6}$$

While some fractionation processes such as those due to CO_2 diffusion into the stomata and carboxylation (see above) are constant and consequently insensitive to climate (McCarroll and Pawellek 2001), others are determined by changes in the environment. Stable carbon isotopes ($\delta^{13}\text{C}$) in tree rings are excellent recorders of variations in climatic conditions as a result of a balance between stomatal regulation due to changes in moisture availability and photosynthetic rates and are a unique and independent resource of long-term information on the physiological status of natural forests. Stable oxygen isotopes ($\delta^{18}\text{O}$) reflect the source of precipitation and also climatic information driven by variations in the vapor pressure deficit that controls stomatal conductance. The

hydrogen isotopes δD are influenced by the same environmental factors as the $\delta^{18}O$ ratios, and so they are the result of similar fractionation process.

A downside of using the isotopes approach as compared to traditional morphological measurements is that stable isotope analyses are relatively more labor intensive to produce and more expensive, typically limiting the total number of measurements that can be reasonably performed. In recent years, however, technical improvements are beginning to successfully circumvent this limitation (e.g., Wieloch et al. 2011). There are several laboratory protocols for isotopic analysis, and here we describe some of the most commonly used methods. The isotopic composition can be measured directly from the wood, but α -cellulose is commonly extracted in order to avoid isotope variations due to other wood components (e.g., lignin or resins). This extraction uses acetic acid, sodium chlorite, and sodium hydroxide (Loader et al. 1997; Loader et al. 2003; Rinne et al. 2005) or nitric acid as described in the Brendel method (Brendel et al. 2000; Anchukaitis et al. 2008). Several methods can be applied for obtaining homogeneous cellulose in relation to its isotopic signature such as mechanical grinding of wood, cellulose freeze-milling with liquid nitrogen or an ultrasonic treatment (Laumer et al. 2009). Pooling can be done with wood from two radii per tree in order to account for isotopic variability around the circumference of a given ring (Leavitt 2010) and to ensure enough material for the analyses. Although pooling with wood from different trees is also a well-accepted method (Leavitt 1984, 2008) that saves time and resources, if applied, there is a lack of information from individual trees that precludes any chance of determining the range of uncertainty of the resulting isotopic site chronology. Finally, the cellulose samples need to be converted to sample gases to be analyzed using isotope ratio mass-spectrometers (IRMS). This gas conversion can be done off-line or online as a part of a continuous flow method that interfaces an elemental analyzer with IRMS. The implementation of online methods has greatly improved the efficiency of the entire process, substantially increasing the possible total number of measurements, a prior limitation to produce long-term records based on isotopic ratios. Stable carbon isotopes (^{13}C and ^{12}C) are measured by combusting small amount of α -cellulose placed into tin capsules to CO_2 in to the elemental analyzer (EA) coupled with an IRMS, whereas samples are placed in silver capsules for measuring stable oxygen isotopes (^{18}O and ^{16}O) using conversion via pyrolysis to CO with a high temperature conversion/elemental analyzer (TC/EA). Some recent technical improvements also can allow measuring both isotopes at the same time using pyrolysis (Knoller et al. 2005). The measurements of hydrogen isotopes (1H and $^2H/D$), both online and off-line, involve some complexities that have prevented progress in technical advancements. As a consequence, the amount of δD data available is still limited in comparison to $\delta^{13}C$ or $\delta^{18}O$ data. Detailed description of mass spectrometry methods, for each stable isotope ratio, can be found in the McCarroll and Loader review (2004).

Wood Anatomy and High-Resolution Imaging

The study of specific features within annual tree rings has also proven to be valuable for understanding and reconstructing links between tree growth and environmental conditions, particularly at intra-annual time scales. Measuring wood characteristics, like the width of the earlywood and latewood for each tree ring, as a source of specific and intra-year climatic information, has recently advanced (e.g., Meko and Baisan 2001; Griffin et al. 2011). On a finer microscopic scale, much information can be attained about past climatic and ecological conditions through careful observation of specific anatomical features within individual rings. This investigation of tree-ring anatomy can be quantified by measuring and counting structural wood components. Quantitative wood anatomy (QWA) combines traditional wood anatomy with dendrochronological techniques and provides temporal records of what often used to be only qualitative information. Many wood anatomists did not traditionally study these two disciplines in unison (Schweingruber 2007; Fonti et al. 2010), but QWA is currently

rising in importance and popularity. Recent improvements in image analysis capabilities have allowed QWA to flourish as a field of research within the past few decades (Fonti et al. 2010). Measurable parameters for conifers have included tracheid cell area and diameter, cell wall thickness, lumen diameter, and number of tracheids, which can also be measured separately for earlywood and latewood (e.g., Vysotskaya and Vaganov 1989; Fillion and Cournoyer 1995; Deslauriers and Morin 2005; Martin-Benito et al. 2013). For angiosperms, the number or density of vessels, conductive area, and vessel area, for example, can be measured (e.g., Woodcock 1989; Fonti and Garcia-Gonzalez 2004; Campelo et al. 2010). Please refer to Fonti et al. (2010) for a comprehensive listing of several wood anatomical studies, including the parameters and climatic signals identified in each study. Such features as traumatic resin ducts and frost rings can also record changes in environmental conditions and can be useful indicators of extreme events in the past (e.g., LaMarche and Hirschboeck 1984; Wimmer 2002; Bollschweiler et al. 2008). Additionally, some wood anatomical studies have identified and described anatomical features in relation to other classical dendrochronological parameters, particularly measurements of density (Yasue et al. 2000; Wang et al. 2002) due to the relation between the latter and characteristics of the cell walls. QWA can complement traditional tree-ring parameters as well as deepen and improve our understanding of linkages between tree growth and the environment over time.

Conclusions

Methods used in the field of dendrochronology have advanced significantly over the past few decades. First, standardization processes designed to obtain as much low-frequency climatic information as possible have advanced through different data treatment methods, such as the RCS and SF methods. Additionally, there are improvements on identifying and standardizing tree-ring series with disturbance signals, particularly for closed-canopy forests. Second, stable isotopes in tree rings continue to emerge as an additional parameter for understanding environmental changes in the past climatic variability, and advances in cellulose extraction and sample processing have recently made isotopic analysis more accessible. In terms of wood anatomy, improvements in image processing technology have resulted in more potential for investigating and quantifying anatomical features in tree rings. All of the aforementioned methodological advances in dendrochronology illustrate that there has recently been significant progress in the field, and it indicates that there will likely be more scientific progress in the years to come.

Cross-References

- [Dendrochronology, Dwellings](#)
- [Dendrochronology, Entomology](#)
- [Dendrochronology, Fire Regimes](#)
- [Dendrochronology, Surficial Processes](#)
- [Dendrochronology, Volcanic Eruptions](#)

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Radiation Dose Rate

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Definition

Radiation dose rate is ionizing radiation energy absorbed per unit of time per unit of mass of the absorbing matter.

Introduction

When radiation travels through matter, it interacts with the matter. As a result of those interactions, the energy of radiation may be absorbed by the matter. Numerous physical processes are responsible for the absorption of radiation energy, depending on the type of radiation. In connection with scientific dating methods, the term dose rate is particularly relevant to trapped charge dating techniques, i.e., luminescence (OSL – optically stimulated luminescence, TL – thermoluminescence) or electron spin resonance (ESR) dating. The determination of absorbed dose and dose rate is the subject of dosimetry which plays a particular role in medicine and the nuclear industry. A comprehensive introduction to dosimetry and associated problems is given by Attix (2004).

In SI units the absorbed dose rate is expressed as 1 Gy/s, where 1 Gy (Gray) is 1 J of radiation energy absorbed by 1 kg of the absorbing matter. In older work, the CGS unit of dose rate of 1 rad/s may be encountered, which is equal to 0.01 Gy/s. The absorbed energy concerns this part of the radiation energy which is used to increase the internal energy of matter, i.e., its temperature.

Ionizing radiation can be divided into two categories:

- Directly ionizing radiation – this includes charged particles (electrons, alpha particles, protons, nuclei, muons) – which deposit energy in the matter through which it travels, through Coulomb interactions.
- Indirectly ionizing radiation – neutral particles (e.g., photons in the form of gamma radiation, neutrons) – which deposits its energy in a two-step process. In the first step, the particles lose some of their kinetic energy in collisions with secondary charged particles (electrons) present in the matter through which the radiation passes, and in the second step, these secondary charged particles lose their energy either through collisions or through radiation emission (e.g., bremsstrahlung – X-rays emitted as a result of deceleration of charged particles).

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The average absorbed dose rate ($\dot{D}$) in a given finite volume (element) of the considered matter is defined by

$$\dot{D} = \frac{\Delta\varepsilon}{\Delta m \Delta t} \quad (1)$$

where $\Delta\varepsilon$ is the difference between radiation energy imparted to the considered volume and radiation energy leaving that volume, Δm is the mass of the considered volume, and Δt is the time over which this energy has been absorbed.

A device which allows the measurement of absorbed dose in a given volume is called a dosimeter. This includes devices for direct measurements (e.g., an ionization chamber with the necessary electronics) or materials whose properties allow storage of radiation energy (e.g., in the form of effects the radiation causes) and a later readout of the accumulated signal and post-determination of the total dose accumulated over the recording time. Examples of the latter may include small chips made of $\text{Al}_2\text{O}_3:\text{C}$ (carbon-doped aluminum oxide) used in OSL dosimetry or capsules with doped lithium fluoride (e.g., LiF:Mg) used in thermoluminescence dosimetry.

Dose Rate Determination

Direct measurements of dose rate within matter are a complex undertaking, especially if the knowledge of distribution on a small scale within the material and with temporal resolution is required (small volume or mass and very short time in Eq. (1)). This is due to the fact that radiation is absorbed differently depending on the density and the atomic number of the matter through which radiation passes and on the type of radiation and its energy. Therefore, if the dosimeter, or dose rate meter, is made of a different material than the one in which we want to determine the dose rate, a need arises to apply conversion calculations. In addition, if different types of radiation, of a range of energies, are present (a so-called mixed radiation field), it is difficult, if not impossible, to calibrate the devices in an absolute fashion to provide readings in Gy/s (or Gy in the case of accumulated dose). Therefore, the application of dosimeters always requires careful consideration in a given experimental setup.

On the other hand, in applications like trapped charge dating techniques, of interest is the average dose rate over the burial time of the dated geological sediment or ceramics rather than momentary dose rate. There exists a possibility to use Monte Carlo simulations to determine the distribution of dose within matter on the basis of simulating the physical phenomena during the passage of radiation through matter and the transport of secondary charged particles in matter (e.g., see Guérin and Mercier 2011, 2012; Nathan and Mauz 2008, example of application in Grine et al. 2007).

Example: Dose Rates Originating from Various Natural Sources

As already mentioned in the introduction, in relation to scientific dating methods, the concept of dose rate has a particular relevance to trapped charge dating techniques. In the Earth's crust, the major radioactive elements present are in the uranium and thorium decay series (natural uranium series consists of 99.29 % ^{238}U and 0.71 % ^{235}U by weight of natural uranium) and potassium (^{40}K). All these isotopes are emitters of gamma rays and beta particles while the two decay series also contain alpha particle emitters. In addition, the Earth is exposed to a constant flux of muons created in upper

layers of atmosphere by very high energy protons traveling from outside the solar system. Hence, the total dose rate experienced by objects on the Earth's surface consists of the contributions of alpha, beta, gamma, and cosmic radiations from these sources. The concentration of U, Th, and K is different at different points of the Earth's crust; hence, the natural dose rate varies from place to place.

Each of the types of radiation has specific issues when its dose rate in trapped charge dating is considered. These issues are related to their range and the way in which they interact with matter. The palaeodose, i.e., the total dose that would be determined by trapped charge dating techniques, is given by

$$P = \text{age} \times \left(kp_{\alpha}\dot{D}_{\alpha} + p_{\beta}\dot{D}_{\beta} + \dot{D}_{\gamma} + \dot{D}_c \right) \quad (2)$$

where p_{α} and p_{β} are factors (values between 0 and 1) related to the size of grains which are being dated (these factors take into account the dose rate being different at the surface of the grains and in their interiors); k is the effectiveness of α particles in inducing a luminescence (or ESR) signal and $\dot{D}_{\alpha}$, $\dot{D}_{\beta}$, and $\dot{D}_{\gamma}$ dose rates of α , β , γ radiation as calculated from the infinite matrix assumption (see next paragraph), respectively; and $\dot{D}_c$ is the cosmic radiation dose rate. The quantity in the brackets in Eq. (2) is the total so-called annual dose, i.e., dose rate expressed in Gy/a or Gy/ka (Gy per annum or kiloannum). It needs to be stressed that the actual radiation dose rate experienced by the grains does not contain the factor k .

The dose rates of alpha, beta, and gamma radiation are determined with the use of the infinite matrix assumption (see Fano 1954; Roesch and Attix 1968; Aitken 1985; and Guérin et al. 2012 for a critical review), i.e., under the assumption that radioisotopes are distributed uniformly in a homogenous matter surrounding the dated material (e.g., grains). In such a case, every portion of the matter absorbs as much radiation energy as it emits, as all the radiation energy is absorbed in the matter. Under this assumption, the specific activities (e.g., in Bq/kg, i.e., parent disintegrations per second per kilogram of matter) of uranium (natural U) and thorium (^{232}Th) chains and potassium (^{40}K) are determined in the material surrounding the dated grains using a chosen method and they are then converted into dose rates using factors derived under the infinite matrix assumption; the latest conversion factor values are given by Guérin et al. (2011, 2012).

In Eq. (2) the term $\dot{D}_c$ denotes the contribution of cosmic radiation attributed mainly to the flux of muons (Prescott and Hutton 1994). The dose rate from cosmic radiation varies with latitude, altitude, and depth below the Earth's surface. This contribution can be calculated from the geographical coordinates and depth of the dated sample. Although often this contribution is small, it is non-negligible, and in environments with low concentrations of radioisotopes considerable, and has to be taken into account.

The dose rate received by dated mineral grains (or artifacts) also depends on the amount of moisture, or, occasionally, carbonates present in the sediment. Water and carbonates attenuate the radiation field, and the more of these substances present, the more strongly attenuated the radiation. The effects of water content may be taken into account as suggested by Aitken (1985) and Guérin and Mercier (2012). The influence of carbonates is more difficult to assess as discussed by Nathan and Mauz (2008) and applied by Grine et al. (2007).

The assumptions of an infinite matrix are not precisely met in real contexts and they have to be considered in determining the annual dose. Particularly, in complex environments, these assumptions ought to be considered carefully. These problems include the presence of highly radioactive grains, different mineral layers of differing radioactivity, and difficult or impossible to determine levels of moisture present in the dated context.

Summary

The concept of dose rate is vital in trapped charge dating techniques with uncertainty or error being directly reflected in the calculated age. The determination of the radiation dose that has been acquired, e.g., by mineral grains, may be a complex task, requiring a range of assumptions to be made.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating, General Principles](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Radiation and Radioactivity](#)

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Luminescence Dating, Dose Rates

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Definition

Dose rate: the amount of energy absorbed by a mineral that can be used as a natural dosimeter per unit time and mass, resulting from naturally occurring radiation both in the sample and its environment. Unit: Gy.a⁻¹ (more commonly given in Gy.ka⁻¹).

Radioactivity: Sources and Types

The focus of dose rate measurements in luminescence dating is to best quantify the amounts of naturally occurring radiation that a dated sample has been exposed to through time. It is well understood that naturally occurring radiation is generated by the decay of radioactive isotopes stored in rocks and sedimentary bodies that make up the Earth's surface. The most common source of such radioactive energy comes from potassium (K), uranium (U), and thorium (Th). ⁴⁰K is a radioisotope of potassium with a half-life of 1.25 10⁹ years; ²³²Th (half-life, 1.41 10¹⁰ years), ²³⁸U (half-life, 4.47 10⁹ years), and ²³⁵U (half-life, 7.04 10⁸ years) are the top members of distinct series of radioelements. ⁴⁰K decays in stable daughter products and is a source of both beta and gamma radioactivity. In comparison to the potassium decay, the radioactive series of thorium and uranium (²³²Th, ²³⁸U, and ²³⁵U) are more complex as they both comprise several alpha and beta emitters (see, e.g., Aitken 1985, for the decay schemes); gamma rays are also emitted in the de-excitation of nuclei, so these series contribute alpha, beta, and gamma dose rates. In an ideal case of a closed system, all radioelements in the series are at equilibrium, i.e., all the members of each chain have the same nuclear activity, defined by the concentration and half-life of the parent. As a consequence, the nuclear activity of all the decay series members from U and Th can be deduced from the concentration, or activity, of the parent. In typical sediments, beta and gamma dose rates contribute roughly two-third and one-third, respectively, of the total dose rates to sand-sized quartz grains; more detailed analysis of the repartition of dose rates can be found in Ankjærgaard and Murray (2007). In some cases (see below), alpha dose rates can also contribute a significant fraction of dose rates.

Beta and gamma radiations have low ionizing powers, i.e., the linear energy transfer is rather small compared to other radiation types such as alpha particles. As a consequence, both beta and gamma dose rates are commonly assumed to have the same efficiency in producing luminescence in a given mineral grain. For example, the amount of luminescence induced by a 1 Gy.ka⁻¹ beta dose rate from ⁴⁰K is assumed to be equivalent to the amount of luminescence induced by a 1 Gy.ka⁻¹ gamma dose rate from the ²³²Th series. Conversely, alpha particles are heavy, highly ionizing particles which saturate along their tracks the electron traps and recombination centers (the energy

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stores of the mineral grain) in the mineral grains at a much faster rate. As a consequence, their efficiency in producing luminescence per unit dose is much lower than that of gamma and beta radiations and has to be taken into account for accurate determination of effective alpha dose rates (see, e.g., Tribolo et al. 2001).

Another source dose rate to mineral grains is that of cosmic radiation. The contribution from cosmic radiation has been tabulated as a function of longitude, latitude, altitude (the two latter factors being the most influent), and burial depth of the dated samples, as the cosmic radiation is attenuated in the ground (Prescott and Hutton 1988). With a focus on burial depth, the contributions from cosmic radiation are classically grouped into a “soft” and a “hard” component. The “soft” component becomes totally attenuated within several tens of centimeters, whereas the “hard” component is capable of penetrating much further into the ground (several meters). Cosmic dose rates generally contribute a low percentage of the total dose rates (<10 % in most cases).

Infinite Matrix Approximation

The most important concept behind the calculation of dose rates in a sedimentary medium is that of the infinite matrix theory (Fano 1954; Roesch and Attix 1968; Aitken 1985). In a radioactive, homogeneous medium, whose dimensions are greater than the range of ionizing radiations, all the energy that is emitted per unit time and mass in the medium is also absorbed in the same medium. In other words, the infinite matrix dose rate in any volume of homogeneous sediment is equal to the rate of energy emitted per unit time and mass in that same volume. Ultimately, from the knowledge of the radioelements’ nuclear properties (nuclear activity, average energy emitted per disintegration), applying this assumption to a known measurement of the concentration of the main radioelements (K, U, and Th) within the volume of sediment allows one to convert these concentrations into infinite matrix dose rates for the homogeneous medium (Guérin et al. 2011).

Measurement

As a consequence, spectrometry techniques are the most widely used techniques to determine dose rates: different available techniques include high-resolution gamma spectrometry, neutron activation analysis (NAA), and inductively coupled plasma mass spectrometry (ICP-MS). In all methods the concentrations of K, U, and Th are determined for dry samples in the laboratory and resultantly converted in infinite matrix dose rates. Another set of techniques, called counting techniques, exploits the proportionality between disintegration count rates and dose rates: for example, beta counting techniques (Ankjærgaard and Murray 2007) and thick source alpha counting (TSAC), or threshold techniques used to derive gamma dose rates from portable field gamma spectrometers (Guérin and Mercier 2011). However, these techniques generally provide less information than spectra analysis, since the different contributions to the calculated dose rates are not individually quantified.

Sample Heterogeneity and Implications for Dose Rate Calculations

The infinite matrix theory assumes homogeneity of the sample environment from a radiation point of view. However, alpha, beta, and gamma radiations travel at different distances within a given

sample and around it, so this uniformity assumption has different meanings. Alpha particles have the ability to travel only short distances within a sample, at typically less than $\sim 20\text{ }\mu\text{m}$. In comparison, lighter beta particles travel up to 2–3 mm and gamma rays travel greater distances, up to 40–50 cm. Departure from homogeneity over these different scales has notable consequences on the accuracy of the corresponding dose rates. It is, therefore, of paramount importance to attempt to avoid the effects of sample heterogeneity in all stages of sample collection. Primarily this is achieved in the field stage by collecting samples from a sedimentary unit that is both uniform in grain size and composition within an area of roughly 1 m^3 and devoid of secondary processes such as pedogenesis, bioturbation, or carbonate replacement, which may act to change the rates of radiation transfer within a given volume of sediment.

One of the most common, and generally unavoidable, sources of dose rate heterogeneities is the presence of water. Primarily, water acts to dilute the concentrations of the radioelements in the sediment, hence requiring an adjustment of the dose rates when determined from laboratory measurements performed on dry samples (as in the case of, e.g., laboratory spectrometry techniques). In addition to this, electron stopping powers and photon interaction cross sections are higher in water than in typical soil constituents. The ratio of these physical quantities provides a correction factor to account for this effect (Zimmermann 1971). Aitken and Xie (1990) have averaged these ratios on the beta and gamma spectra in typical sediments, and more recently Nathan and Mauz (2008) have proposed new working values based on Monte Carlo simulations.

The general dosimetric concepts presented so far apply to most minerals dated by luminescence. However, constituent rock and/or mineral grains that make up a sedimentary unit have their own distinct characteristics in terms of dose rate determination. For example, flints usually have homogeneous spatial distributions of radioelements at the scale of both alpha and beta radiations (Schmidt et al. 2013) and are thus simple dosimeters from an alpha and beta dose rate calculation perspective. However, such rocks are often embedded in sediments of different characteristics, both in terms of chemical composition and radioactivity. Given the range of gamma rays (40–50 cm), gamma dose rates to rock samples thus mainly depend on the characteristics of their environment. As a consequence, direct measurements of gamma dose rates in the field (using either field gamma spectrometry techniques or artificial dosimeters) are often preferred to determine gamma dose rates to such samples; an alternative consists of determining gamma dose rates from sediment samples taken close to the rock samples.

Many mineral forms such as quartz and potassium feldspar that are commonly utilized in luminescence dating are more complicated in terms of dose rate determination. This is a result of their chemical composition and grain dimensions which ultimately break the key infinite matrix assumption of sample homogeneity. With focus on alpha and beta dose rate contributions, quartz grains contain very few radioelements (Vandenberghe et al. 2008) and thus represent cold spots in sedimentary matrices. In comparison, due to their high potassium content, feldspar grains act as radioactive sources themselves, which generate an internal dose rate that must be accounted for in final dose rate calculations. Internal dose rate to potassium feldspar grains can be calculated using their potassium content (Huntley and Baril 1997) together with dose rate conversion factors (Guérin et al. 2011). The self-dose fraction of the infinite matrix dose rate has been tabulated by Guérin et al. (2012). The small but significant contribution from ^{87}Rb can be calculated according to Readhead (2002) and Huntley and Hancock (2001). Finally, the diameter of the mineral (quartz and feldspar) grains commonly studied in luminescence (typically $\sim 100\text{--}250\text{ }\mu\text{m}$) is not negligible compared to the range of beta particles. As a consequence, the grains attenuate beta radiation from the surrounding matrix. Grain-size-dependent attenuation factors of external beta dose rates from the environment can be found in Guérin et al. (2012).

Due to the small range of alpha particles, they get strongly attenuated in sand-sized grains and their contribution is negligible $\sim 20\text{ }\mu\text{m}$ in the grains; furthermore, homogeneity of the environment of the grains is very difficult to assess at this scale. It is thus common to bypass potentially inaccurate dose rate determinations, to avoid working with alpha dose rates. For that matter, coarse grains are often treated with hexafluorosilicic acid (HF) to remove the outer rim of the grains, which has been irradiated by alpha particles, and thus eliminate the alpha dose rate contribution. For smaller grains, however, where chemical etching is not possible, a proper assessment of alpha dose rates and of alpha particle efficiency in luminescence production is crucial.

Current Investigations

The infinite matrix assumption is a very powerful tool in deriving dose rates from rocks and sedimentary units. Although fundamentally set in principle, it does allow for small departures from the concept of sample homogeneity through variations in water content and grain size. In particular, the infinite matrix assumption has been of significant use when applied to the dating of ceramics, where quartz grains are included in a uniform clay matrix at the scale of alpha and beta radiations. However, the current focus of luminescence dating has shifted to the dating of sediments where the requirements of the infinite matrix assumption are rarely met. For example, the presence of sand-sized feldspar is problematic in deriving infinite matrix dose rates, due to their non-negligible size compared to beta ranges which acts to absorb some amount of radiation and hence reduce the relative levels of radiation in other localized minerals.

Furthermore, the use of grain-size attenuation factors to calculate beta dose rates to quartz grains is based on the assumption that quartz grains represent nonradioactive inclusions in an otherwise uniform, radioactive matrix (as is the case, e.g., of sand-sized quartz grains surrounded by clay in pottery). In a sand dune, where quartz grains are the main constituent of the sediment, such a uniform matrix surrounding the grains does not exist; small grains will attenuate beta radiation less than coarse grains, but this is a relative effect, and therefore, the use of classical dose rate attenuation factors is not suited for absolute dose rate calculations (see Guérin et al. 2012).

Because of these problems related to spatial variations in dose rates, especially at the range of beta particles, some research in the field is devoted to the development of numerical and experimental methods to characterize and quantify sources of radioactivity (see, e.g., Rufer and Preusser 2009). In particular, the spatial distribution of dose rates, in relationship with the distribution of natural dosimeters (e.g., quartz grains), is a field of special interest. It is well known that some of the dispersion in single grain OSL equivalent dose distributions arises from heterogeneities of radioactivity at the scale of beta radiations: grains close to a beta source such as a potassium feldspar grain will receive a higher dose rate during burial than grains more distant from such sources. However, until now only few models have been proposed to quantify dose rate distributions at the single grain level. Mayya et al. (2006) modelled such distributions arising from the presence of potassium feldspar grains in sand made of $200\text{ }\mu\text{m}$ quartz grains; they have shown that potassium concentration in such environments is an important factor because as the potassium content is decreased, the average distance between source (potassium feldspar) and dosimeter (quartz) is increased. As a result, few grains located close to the sources will receive high dose rates, whereas most quartz grains will receive small beta dose rates, which leads to dispersion in dose rate distributions to single grains of quartz. However, more focused studies are required in order to identify the different factors driving the dispersion of dose rates. Such studies would then allow direct comparisons between equivalent dose and dose rate distributions at a single grain level and

thus allow distinguishing the different factors of dispersion in equivalent doses, for example, insufficient bleaching at the time of sediment deposition.

At a gamma dose rate scale (10 cm and more), important spatial variations may occur, for example, at the interface between sediment and bedrock or between sediment and air when samples are taken close to the surface. The presence of rocks in sediments may also influence gamma dose rate to luminescence samples. For example, it is well known that limestone is generally less radioactive than other sediment types such as clay. In complex environments where calcareous lumps are found in fine sediments richer in radioelements, Brennan et al. (1997) have thus recommended using in situ gamma dose rate measurements to obtain representative measurements.

In closure, one of the main problems in dose rate estimation lies in the evolution of this physical quantity with time: present-day dose rates may not be representative of the sample history. Water circulation, for example, can induce movement of radioelements in sediments. ^{238}U can be soluble in some environments as well as ^{226}Ra and this can cause disequilibrium in uranium series. ^{222}Rn has a short half-life (3.8 days) and is gaseous, so it can easily escape from the ground when surface is exposed to open air. High-resolution gamma spectrometry and alpha spectrometry can reveal differences in the activity of different members of the decay chain; in such cases, different scenarios for the origin of the disequilibrium can be investigated (e.g., Guibert et al. 2009) and then dose rate variations in time can be accounted for.

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Luminescence Dating, Deep-Sea Marine and Lacustrine

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Synonyms

Infrared-stimulated luminescence (IRSL); Optical dating; Optically stimulated luminescence (OSL); Thermoluminescence (TL)

Definition

Luminescence dating: A family of chronologic methods typically applied to the commonly occurring minerals quartz and feldspar, which exploits a time-dependent signal that builds up in mineral grains by exposure to naturally occurring ionizing radiation (principally from uranium, thorium, and potassium). The methods assess the time elapsed since these mineral grains were last exposed to sunlight or to heating. In the case of marine and lacustrine sediments, the event being dated is the last exposure to sunlight, i.e., typically the time of deposition of the sediments.

Deep-sea, marine: Of or pertaining to the deeper parts of the sea or ocean (as opposed to shallow waters and coasts).

Lacustrine: Of or pertaining to lakes.

Introduction

Despite the fact that marine sediments were among the first sediments from which a luminescence signal was observed (Wintle and Huntley 1979), subsequently little work has been done using luminescence to date marine sediments. Similarly, surprisingly little work has been done to apply luminescence procedures to date lacustrine deposits, in spite of the rapid development, the widespread uptake, and the improved accuracy and precision of luminescence dating when applied to a wide variety of other depositional settings. The reasons behind this reluctance to use luminescence techniques to provide ages for marine and lacustrine sediments share some common links, and the challenges faced in dating these water-lain sediments are similar. It is therefore appropriate that these two depositional environments are considered together.

Historical Overview of Luminescence Dating in Deep-Sea Marine and Lacustrine Environments

Deep-Sea and Marine Sediments

The term “luminescence dating” is a broad concept which has itself developed over time, and today the term actually incorporates a family of methods which have been developed over the last

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~35–45 years for dating in different settings including sedimentary environments. These various luminescence dating methods use different signals (some of which are stimulated by heat, “thermoluminescence” (TL), and some by light, “optically stimulated luminescence” (OSL)) and different measurement protocols to determine the final numerical age estimate. A more detailed consideration of luminescence dating (see “► [Luminescence Dating](#)”) and its history (see “► [Luminescence Dating, History](#)”) are given elsewhere in this encyclopedia. However, it is interesting to note here that the potential of TL signals from quartz and feldspars to derive a numerical age for the time of deposition of marine sediments was first noted in the western literature using marine sediments. Wintle and Huntley (1979) observed an increasing TL signal with increasing depth for a core from the Crozet Plateau in the Antarctic Ocean and recognized that this TL signal was coming from inorganic sediment. Furthermore, they noted that exposure to sunlight could act as a mechanism for resetting the TL signal prior to deposition of the sediments. Comparing the TL ages generated against independent age control, Wintle and Huntley (1979) concluded that the findings were “sufficiently encouraging to suggest that the method is basically sound.” Following this pioneering work, TL was then rapidly applied to terrestrial sediments, particularly loess (see entry for “► [Luminescence Dating, Loess](#)” in this encyclopedia), but it was to be more than 20 years until further work was done in deep-sea or marine settings using luminescence signals of any kind.

In the intervening 20 years, luminescence dating underwent a series of radical transformations (see “► [Luminescence Dating, History](#)”), the most critical being the development of optical stimulation to yield a signal appropriate for dating sediments, and the development of sensitivity-corrected methods for measuring the luminescence signal from single aliquots (e.g., the single-aliquot regenerative dose (SAR) measurement protocol of Murray and Wintle (2000), which has subsequently been adapted and developed for various luminescence signals and materials). Following the introduction of the SAR protocol for quartz, and comparison of the ages generated against independent age control (e.g., Murray and Olley 2002; Rittenour 2008), confidence grew in the OSL signal from quartz for dating and in the ability to look at complex equivalent dose (D_e) distributions; attention could now be turned to more challenging environments, including the marine realm.

Stokes et al. (2003) were the first to apply a SAR OSL measurement protocol to quartz prepared from deep-sea marine sediments, studying cores taken from the Western Arabian Sea. The fine-grained quartz ages generated were in agreement with independent age control provided by radiocarbon, tephrostratigraphy, and paleoecological data (Stokes et al. 2003). The fine-grained (4–11 μm diameter) quartz was believed to be eolian (i.e., wind-blown) in origin, and as such is likely to be well bleached prior to deposition. Using fine grains for OSL dating precludes the possibility of investigating the degree of bleaching because of the large number ($>10^5$) of grains on each aliquot. In spite of this, it is interesting to note that Stokes et al. (2003) still observed $>4\%$ of aliquots with D_e values >3 standard deviations from the mean estimate, and they used this rather crude approach to screen and remove outlying D_e data; today a more sophisticated statistical approach would be taken (e.g., the Minimum Age Model, Galbraith et al. 1999; see “► [Luminescence Dating, Single Grain Dose Distribution](#)”). Such an approach was taken by Olley et al. (2004) who examined the degree of bleaching of sediments from the eastern Indian Ocean using single grains of fine-sand-sized (60–70 μm) quartz. In spite of being eolian in origin and having relatively long transport distances (and it would be thought, ample opportunity for bleaching), some samples were incompletely bleached on deposition. However, following appropriate statistical treatment, the single-grain quartz OSL ages generated were in agreement with independent age control provided by radiocarbon, between ~1,500 and 50,000 years ago (Olley et al. 2004). If problems of incomplete bleaching prior to deposition are found to be an issue in these nonpolar marine settings where eolian transport can dominate, it should perhaps come as little surprise that problems of incomplete

bleaching and age overestimation have also been reported in polar marine settings (e.g., Jakobsson et al. 2003; Berger 2006), where daylight can be restricted and where transport pathways are more complex and can occur in association with ice and turbid water. Nevertheless, some of these OSL ages have been found to be in agreement with the expected ages (e.g., Jakobsson et al. 2003). However, it was not possible to develop criteria based on luminescence evidence alone by which accurate and inaccurate luminescence ages could be distinguished.

More recently, quartz grains of fine-silt (4–11 μm), coarse-silt (~ 38 –63 μm), and fine-sand (63–90 or 90–125 μm) size have been analyzed in nonpolar deep-sea marine settings, and these yield SAR OSL ages which are typically in agreement with independent age control or expected ages, e.g., the Sea of Okhotsk (Sugisaki et al. 2010a, b) and the south Bohai Sea, China (Yi et al. 2012a, b). A notable exception is the work undertaken in the south Bohai Sea where radiocarbon ages of 38–44 cal kyr BP have been used to assign a particular sedimentary unit to Marine Oxygen Isotope Stage (MIS)-3 (Liu et al. 2009), while OSL ages suggest that the unit actually relates to MIS-5 (Yi et al. 2012b) and hence imply that the radiocarbon ages may be at the limit of the method and thus unreliable. This example highlights the potential value of luminescence dating in any depositional setting where it can be used to extend the numerical chronology for a sedimentary sequence beyond the upper (and indeed lower) limit of radiocarbon dating. Where agreement can be established between luminescence ages and any other independent chronology in a time span clearly appropriate for both methods (e.g., in Holocene sediments from the south Bohai Sea; Yi et al. 2012b), then there is additional confidence that as one chronometer approaches its limit, then the second chronometer can be used to extend the chronology.

In carbonate-restricted zones such as high-accumulation-rate deposits where there is a lack of biogenic material, and in deep areas of the oceans below the carbonate compensation depth (CCD), there is even greater incentive to use luminescence techniques to generate a numerical chronology. Given the relatively limited number of luminescence dating studies conducted thus far in marine settings, further studies are probably required in order to build up confidence in the ability of luminescence dating to generate accurate ages in settings where no independent chronology exists. However, the initial studies that have been conducted are extremely promising.

Lacustrine Sediments

Lakes preserve some of the best terrestrial records of climate and environmental change on Earth, containing numerous proxy records which can be seen to vary over time. Surprisingly little work has been done to apply luminescence techniques to date lacustrine sediments. Instead, such sediments have hitherto primarily been dated using radiocarbon techniques, and extrapolation is frequently used to infer the age of sediments beyond ~ 40 –50,000 years ago (e.g., Burnett et al. 2011). However, given the potentially long time period over which lake sediments can accumulate, and the comparatively short time range over which radiocarbon can be applied, there is tremendous scope for the use of luminescence techniques for dating lacustrine deposits.

The reluctance to apply luminescence techniques to date lacustrine sediments is probably linked primarily to concerns over the degree of bleaching of the sediments prior to deposition. For this reason, where luminescence techniques have been used to date lacustrine sediments, it is primarily lake shoreline deposits (rather than lake floor sediments) that have been dated thus far (e.g., Burrough et al. 2009). These concerns over incomplete bleaching of the luminescence signals prior to deposition were particularly pertinent in the early days of luminescence dating when TL signals were used, because the TL signal is known to bleach much more slowly in nature than the OSL signal. Additionally, bleaching in the water column adds an extra layer of complication due to the turbidity of the water and the attenuation of the spectrum with increasing depth through the water

column. Lake morphology (i.e., shape) is therefore likely to be an important factor in determining the success of a lacustrine luminescence study; for example, an early study by Berger et al. (1987) demonstrated that large lakes with broad, low-gradient lake floors were likely to be most appropriate. In spite of these concerns over bleaching prior to deposition, particularly using TL signals, the successful application of luminescence dating of lacustrine sediments is demonstrated by Berger and Anderson (1994) for Squirrel Lake, Alaska, where TL and radiocarbon ages were found to be in agreement for the upper 3 m of sediment, which was within the range of radiocarbon dating; beyond this, a further 11 m of sediment was dated using TL with the maximum age being 125 ± 31 ka (Berger and Anderson 1994). The IRSL signal from feldspars bleaches more rapidly than the TL signal, and for this reason, Berger and Doran (2001) favored the IRSL signal for dating lacustrine sediments from Lake Hoare, Antarctica, which gave IRSL ages that were younger than TL ages for corresponding samples. Even though these IRSL ages were younger than the TL ages generated, there is still some question as to whether the IRSL signal was completely bleached prior to deposition because examination of a modern analogue sample (which should give an age which is essentially zero years) returned an age of ~600 years. The OSL signal from quartz bleaches even more rapidly than that of feldspar and also offers the advantage that it does not suffer from anomalous fading (which can cause age underestimation in feldspars), and hence today since the advent of SAR methods (Murray and Wintle 2000), quartz would probably be the mineral of choice for dating lake sediments. An example of the successful use of quartz OSL dating to determine the ages of lacustrine sediments is provided by Long et al. (2011) for Qingtu Lake, in northern China, where good agreement was obtained between OSL ages from coarse-silt-sized quartz and radiocarbon ages derived from shell fragments and organic-rich bulk sediments.

Although the quartz OSL signal bleaches most rapidly of all the commonly used signals from the family of luminescence dating techniques, this fast component OSL signal is also the fastest to saturate in nature, i.e., it has the youngest upper limit for dating (~150 Gy (Chapot et al. 2012), which is likely to correspond to a maximum age for lacustrine sediments of ~130 ka). For example, Lowick et al. (2010) and Lowick and Preusser (2011) generate fine-grained quartz OSL ages that are in agreement with independent biochronologic evidence to ~140 Gy (which in this study corresponds to an age of only ~70 ka), but beyond this the OSL ages are increasingly underestimated. For this reason, Zander and Hilgers (2013) explored the use of various different luminescence signals to date their Middle- to Upper-Pleistocene sediments (~145–760 ka) from Lake El'gygytgyn, Russia. In this study, the quartz OSL signals were saturated and hence gave ages which significantly underestimated the expected age based on magnetostratigraphy, and the IRSL signals measured at 50 °C from polymineral fine grains also gave rise to age underestimations throughout the study for similar reasons. The thermally transferred OSL ("TT-OSL") quartz ages were also unsatisfactory as they were found to be of variable reliability. However, ages generated using a post-IR IRSL₂₉₀ measurement protocol (Thiel et al. 2011) which minimizes anomalous fading were in agreement with the expected ages back to ~465 ka and potentially even to ~760 ka (Zander and Hilgers 2013).

Practical Considerations, Concerns, and Benefits of Using Luminescence Techniques to Date Deep-Sea Marine and Lacustrine Sediments

Several practical considerations and concerns have contributed to the slow uptake of luminescence techniques for dating deep-sea marine and lacustrine sediments. However, there are several key benefits offered by luminescence dating which it can be argued now outweigh these concerns.

Practicalities

Deep-sea marine and lake floor sediments are typically obtained as cores, often requiring deep drilling to obtain them. This logistically complex and hence also relatively expensive method of retrieval leads to further complications. Being taken in cores, the material is often relatively limited in terms of the sample size available. The wide variety of proxies available from lake cores also means that the precious core material is required for numerous different analyses, which again restricts the amount of core material available for any one technique. In many studies, cores are often split and logged and exposed to daylight prior to sampling for luminescence dating. While light-exposed cores can still be successfully sampled for luminescence dating (by removing the outer, light-exposed portions of the core which can be used for dose-rate determination), it should be noted that X-ray scanning prior to sampling for luminescence can add a radiation dose to sample material, potentially leading to erroneous age determinations (Davids et al. [2010](#)).

Concerns

One of the principal concerns regarding the use of luminescence dating in deep-sea marine and lacustrine sediments is the accurate assessment of the water content over the post-depositional history of the sediments; this is important because water attenuates the radiation dose reaching the sediment grains and hence influences the age determination. Uncertainty in the water content is typically the largest single source of uncertainty in luminescence ages generated for deep-sea marine and lake floor sediments. The water content of such water-lain sediments can be extremely variable through the sedimentary sequence and also changes over time, with the lowermost sediments becoming increasingly compacted as new sediments accumulate above, causing dewatering and hence a reduction in water content over time. Compaction of the sediments can also occur on retrieval of sedimentary cores, and care must therefore be taken to assess the degree of compaction during the drilling process to facilitate the reconstruction of water content after sampling. It is also important to consider the changing depth of water (and sediment) above the chosen sample location within the sedimentary profile because it will influence the cosmic dose rate (and the dose rate from adjacent sediments) reaching the sample over time.

Another key concern is the degree of bleaching of any preexisting luminescence signal prior to deposition in deep-sea marine and lacustrine settings; investigating this is particularly difficult in these settings due to the typically fine-grained nature of the sediments precluding the determination of D_e values for individual grains which would otherwise be used to assess the degree of bleaching. An alternative approach is to compare the D_e values obtained using different luminescence signals from the same sample and exploit the different bleaching rates of the luminescence signals as a means of identifying incompletely bleached sedimentary units. For example, Buylaert et al. ([2013](#)) proposed using the ratio of IR_{50} and $pIRIR_{290}$ D_e values throughout a lacustrine sediment profile at Laguna Potrok Aike, Argentina, to screen out incompletely bleached samples; the ages which passed this screening criterion (29 ages out of 47 analyzed) are chronostratigraphically consistent and show good agreement with independent age control.

A further concern is the geochemistry of deep-sea marine and lacustrine settings, which can complicate the assessment of the dose rate. In such cases, the assumptions typically made regarding the presence of secular equilibrium in the uranium- and thorium-decay series chains and thus a constant dose rate (Gy/ka) over time would not hold true, and hence a more detailed assessment of the dose rate over time would need to be conducted to account for the unsupported and supported radionuclides (e.g., Stokes et al. [2003](#)).

Benefits

Given the concerns outlined above, and the relatively small number of luminescence studies in deep-sea marine and lacustrine settings thus far, it would seem prudent for new studies to have some form of independent age control for verification of the luminescence ages generated. However, this will not be possible in all cases, and indeed the lack of age control in these settings is a key motivation for applying luminescence dating here. Where other chronologic evidence does exist, it can sometimes be complicated by problems within that technique itself (e.g., radiocarbon reservoir effects). Notwithstanding these issues, luminescence dating of deep-sea marine and lacustrine sediments is becoming an increasingly attractive prospect, particularly given advances in equipment and methodology since the year 2000, and also in the accuracy and precision of the ages generated. Luminescence dating offers a number of internal quality control checks that can be performed to offer assurance of the suitability of the signals used for dating (e.g., Roberts 2008), and unlike some other methods, it is not beset by issues of calibration. Luminescence dating is also an attractive method because the two minerals principally used for dating (quartz and feldspar) are very common, so it is rarely problematic to find sufficient material for dating. Furthermore, luminescence dating provides a numerical chronology and hence allows the assessment of accumulation rates through long sedimentary sequences without the need for extrapolation and the inherent assumption of a constant accumulation rates over time periods typically from the present day to 10^5 years.

Summary and Conclusions

Relatively few studies of deep-sea marine or lacustrine sediments have taken place using luminescence dating. The most successful approach demonstrated thus far is the use of quartz OSL signals for dating, measured use of a single-aliquot sensitivity-corrected method such as SAR, although newly developed post-IR IRSL methods developed to minimize anomalous fading in feldspars also show great promise. The luminescence ages generated tend to be in good agreement with the independent age control. Given the difficulties of dating marine and lacustrine sediments using many other methods (e.g., “► [Sediments, Marine \(Palaeomagnetism\)](#),” “► [Lacustrine Environments \(\$^{14}\text{C}\$ \)](#),” “► [\$^{210}\text{Pb}\$ Dating](#),” “► [\$^{226}\text{Ra}\$ Dating, Sediment](#),” “► [Carbonates, Lacustrine, \(U-Series\)](#),” “► [Carbonates, Marine Carbonates, \(U-Series\)](#),” “► [Sedimentation Rate, Marine \(U-Series\)](#)”), and the particular problems that can be associated with the use of radiocarbon in some settings (► [\$^{14}\text{C}\$ Dating](#)), luminescence dating could potentially make an important contribution to the study of deep-sea marine and lacustrine sediments in the future.

Cross-References

- [\$^{14}\text{C}\$ Dating](#)
- [\$^{210}\text{Pb}\$ Dating](#)
- [\$^{226}\text{Ra}\$ Dating, Sediment](#)
- [Carbonates, Lacustrine \(U-Series\)](#)
- [Carbonates, Marine Carbonates, \(U-Series\)](#)
- [Feldspar](#)
- [Lacustrine Environments \(\$^{14}\text{C}\$ \)](#)
- [Luminescence Dating](#)
- [Luminescence Dating, History](#)

- [Luminescence Dating, Single Grain Dose Distribution](#)
- [Luminescence, Coastal Sediments](#)
- [Quartz](#)
- [Sedimentation Rate, Marine \(U-Series\)](#)
- [Sediments, Marine \(Palaeomagnetism\)](#)

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Sediment, ESR

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Synonyms

ESR dating of sediment; ESR dating of sedimentary quartz

Introduction

As quartz is the most common mineral forming the rocks of the earth surface, its dating is of potential value. Electron spin resonance (ESR) dating of sedimentary quartz has many applications in geology and archaeology. The first studies on ESR dating of sedimentary quartz were done by McMorris in the early 1970s and then by Yokoyama et al. (1985) and Tanaka et al. (1985) and summarized by and Ikeya (1993). During the past two decades, our knowledge about the ESR dating of sedimentary quartz has improved, and this method can now be routinely used for dating alluvial sedimentary quartz deposits.

Paramagnetic Centers Used for Dating of Quartz

The silicon atom, Si, is inside four oxygen atoms forming a tetrahedral SiO_4 . In case of silica, or quartz (SiO_2), each oxygen atom is bonded with two Si atoms to form a three-dimensional network in a crystalline form. Impurity-associated defects gives ESR signals associated with impurities such as substitutional tetravalent ions (Ge^{4+} and Ti^{4+}) and trivalent ion (Al^{3+}) as well as interstitial monovalent cations, M^+ (H^+ , U^+ , and Na^+) (see Fig. 1; Weil 1984; Ikeya 1993). These paramagnetic centers, radiosensitive and with a high thermal stability, can be used as dosimeters, though the use of the Ge^{4+} center remains unclear (see below).

Formation of Al Paramagnetic Centers

In the SiO_2 lattice, trivalent aluminum ion Al^{3+} is easily substituted at a Si^{4+} site. The principle of ionic charge neutrality in an ionic crystal requires a charge-compensating monovalent cation interstitial. In this case, a monovalent cation M^+ such as Li^+ , Na^+ , and H^+ at the interstitial site is associated with Al^{3+} as a charge compensator and gives rise to a $[\text{AlO}_4/\text{M}^+]^\circ$ center. When the charge-compensated $[\text{AlO}_4/\text{M}^+]$ traps a hole created by ionizing radiation at room temperature on one of the two long-bonded oxygen neighbors, the cation M^+ diffuses away leading to $[\text{AlO}_4/\text{h}]^\circ$, where h is a hole trapped in a nonbonding 2p-orbital of oxygen located adjacent to the substitutional aluminum (O'Brien 1955; Hitt and Martin 1983 in Ikeya 1993).

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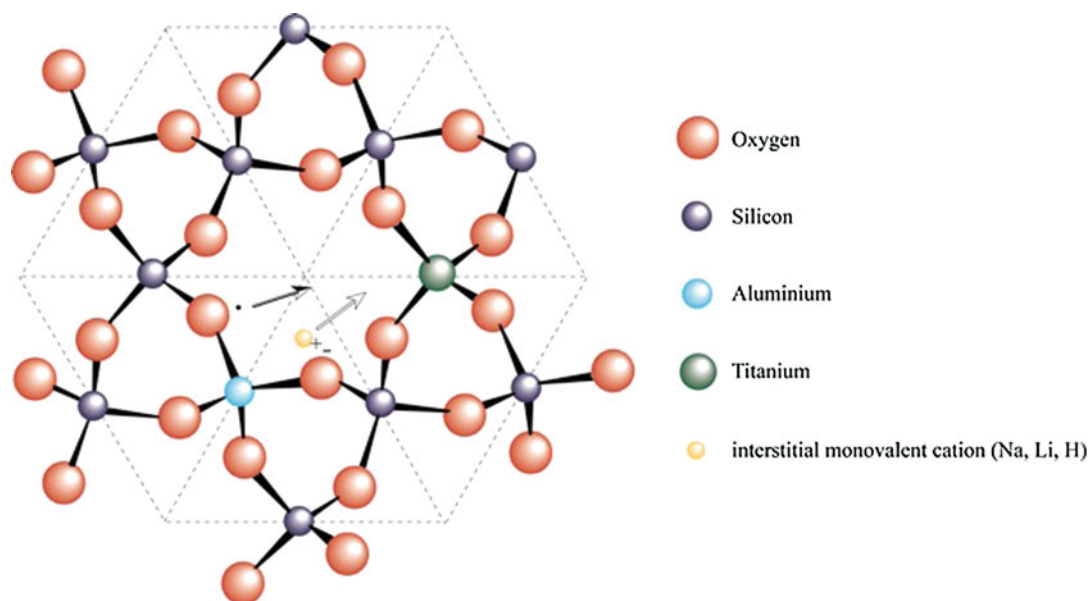


Fig. 1 Impurity-associated defects present in the SiO_2 lattice

Formation of Ti and Ge Paramagnetic Centers

Ge^{4+} or Ti^{4+} substitutes for a Si^{4+} site in the SiO_2 lattice, but its electron affinity (ionization potential) is considerably larger, resulting in trapping of an electron created by ionizing irradiation to form $[\text{GeO}_4/\text{TiO}_4\text{-e}^-]^-$ in the SiO_2 lattice. The total charge of the center is -1 , and thus Ge^{3+} or Ti^{3+} at a Si^{4+} site in an SiO_2 structure has a negative effective charge, attracting an interstitial monovalent cation M^+ such as H^+ , Li^+ , or Na^+ , to form stable $[\text{GeO}_4/\text{M}^+]^\circ$ or $[\text{TiO}_4/\text{M}^+]^\circ$ at room temperature (Andersen et al. 1974 in Ikeya 1993).

Paramagnetic Center Features

Al center is commonly employed for dating as it is a radiosensitive center with a high saturation dose and it is one of the most thermally stable radiation-induced centers in SiO_2 . The ESR signal related to the aluminum can be detected in all natural quartz and used for dating sedimentary of quartz grains deposited during all the Plio-Pleistocene period (McMorris 1971; Yokoyama et al. 1985; Toyoda and Ikeya 1991; Falguères et al. 1991; Laurent et al. 1998; Toyoda and Falguères 2003; Lin et al. 2006).

Ti–Li and Ti–H center can be detected in almost all sedimentary quartz. The saturation of the Ti–H center is rapidly reached (Beerten et al. 2006; Tissoux et al. 2007, 2008). This implies that Ti–H center can be used only for the dating of samples with low palaeodoses (Upper Pleistocene deposits, or older in case of very low annual dose). Ti–Li center could be used for dating sediments of Lower Pleistocene age (Rink et al. 2007; Liu et al. 2010).

It is possible that the Ge center could be employed over the same range of ages as the OSL dating method. However, the ESR Ge signal is rarely observed in the natural samples, although growing with small artificial irradiation doses, suggesting that it is not stable over geological time scales (Rink 1997).

Ge center can be detected by ESR at room temperature, whereas Al and Ti center signals are observed at low temperature (Fig. 2).

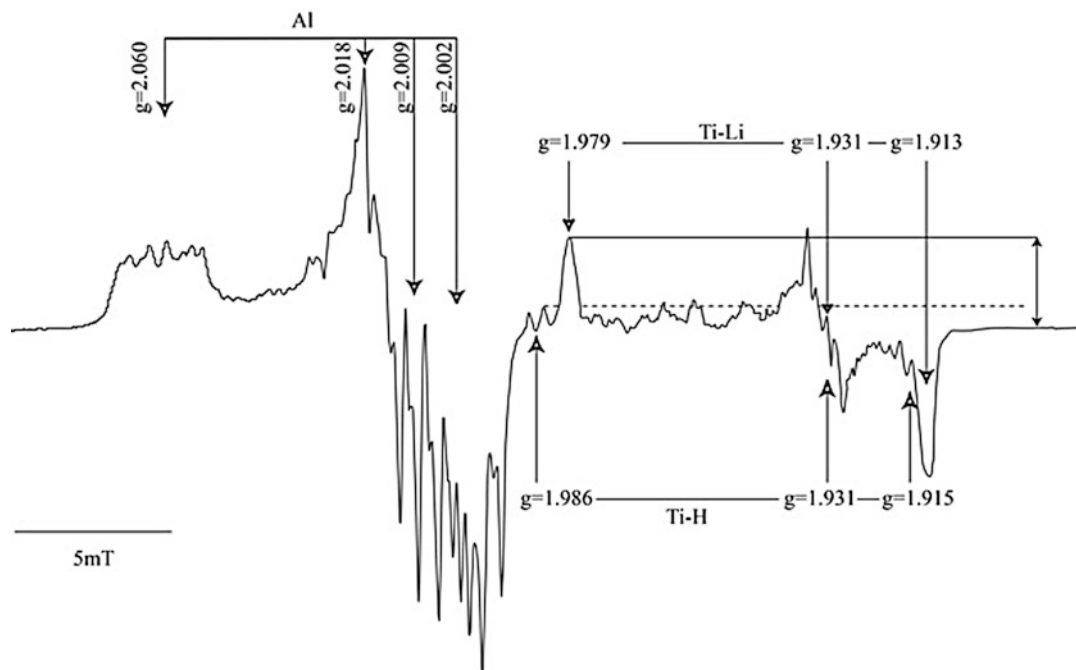


Fig. 2 *Al* and *Ti* center measured samples measured with a JEOL PX-2300 ESR spectrometer. Temperature 80 K; microwave power 5 mW; width of the magnetic field 10 mT; modulation amplitude 0.1 mT; time constant 0.03 s.; frequency 100 kHz (After Tissoux et al. 2008, modified)

Bleaching

When dating sedimentary quartz, the geological or archaeological events have to be dated, not the quartz growth. Thus, a zeroing of the quartz geochronometer is necessary before the time of deposition of the sedimentary sequence. This zeroing is also named “bleaching.” The bleaching occurs when the energy brought to the quartz grain is sufficient to release the electron trapped in the defects (activation energy). This energy can be brought by pressure, light exposure, or heat, and the exposure has to be long enough for a maximal release of the trapped electron. Otherwise, a residual dose is inherited from the primary history of the quartz, leading to an overestimation of the dose acquired during the depositional history of the quartz grain.

Regarding marine, alluvial, or aeolian sediments, an optical bleaching by sunlight of the light-sensitive paramagnetic centers of quartz occurs during the transportation of the quartz grain by water or by wind, before deposition in the sedimentary sequence (Fig. 3).

Many authors investigated the behavior of some paramagnetic centers of quartz when they are exposed to natural or artificial light (Brumby and Yoshida 1994; Walther and Zilles 1994; Yoshida 1996; Tanaka et al. 1997; Toyoda et al. 2000; Voinchet et al. 2003; Tissoux et al. 2007, 2012).

They observed that Al centers of quartz cannot be totally bleached by exposure to the sunlight. An ESR residual dose, related to Al centers, is observed in quartz after a maximal optical bleaching and is generated by the presence of deep aluminum traps in the crystal, which cannot be reset by solar light. This residual dose must be determined for all the sedimentary quartz when ESR geochronology studies are performed. Bleaching experiments indicated that several weeks of exposure were necessary to obtain a maximal bleaching of the Al center (plateau value); the Ge center can be totally bleached in 3 h of exposure by simulated solar light; the Ti–Li center can be

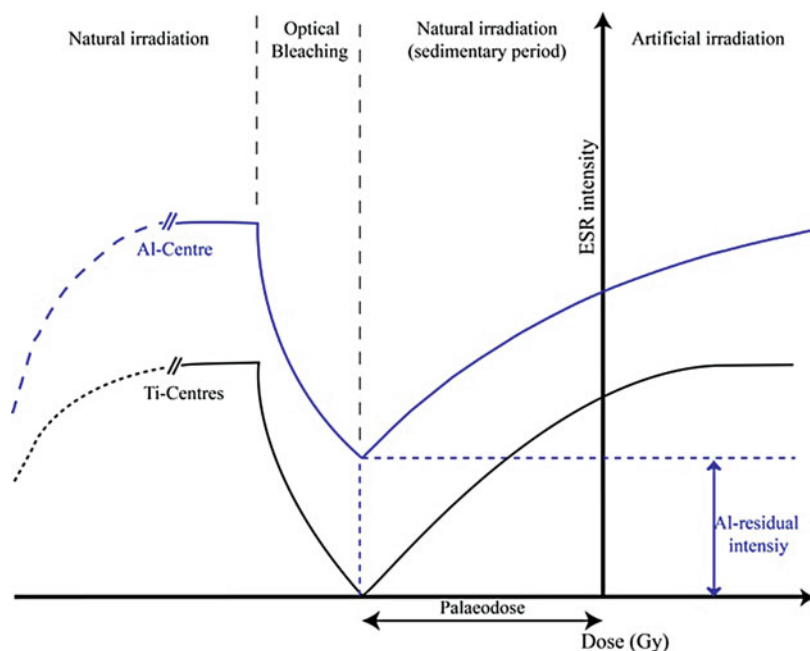


Fig. 3 Optical bleaching history of *Ti* and *Al* centers in sedimentary quartz

totally bleached after a time of exposure similar to the one of Al center, whereas Ti–H center needs less than half the time to be totally bleached.

ESR Dating of Optically Bleached Fluvial Quartz Deposits

The ESR dating of alluvial quartz is based on the hypothesis of ESR trap resetting by sunlight during the transport phase in the river prior to the sediment burial. The calculated age does not correspond to the quartz crystallization but to the time elapsed since the quartz deposition in the alluvial formation.

The exposure time necessary for a maximal bleaching during transport by the river seems to be a very long exposure in natural conditions. However, studies of modern sediments deposited in sandy bars show that the maximum bleaching is effectively reached for Al center at few kilometers from the river’s spring (Voinchet et al. 2007). Liu and Grün (2011) conclude that tumbling due to fluvial transport may take a part in the resetting of the ESR centers. ESR dating of fluvial deposits has been then successfully applied using Al center of quartz (Yokoyama et al. 1985; Laurent et al. 1994; Voinchet et al. 2003, 2004). “Absolute” chronologies of alluvial systems could then be established with strong implications in archaeology (Bahain et al. 2007; Voinchet et al. 2010; Despriée et al. 2011).

ESR Dating of Optically Bleached Aeolian Quartz Deposits

Signal resetting by sunlight prior to burial is a crucial assumption in electron spin resonance (ESR) dating of sediments. This resetting process was successfully tested for Ti–Li and Ti–H signals of quartz from a contemporary desert surface deposit, demonstrating the potential of using the Ti–Li and the Ti–H centers in quartz for dating fossil sediments from similar environments (Beerten and

Stesmans 2005). On the contrary, optical bleaching experiments showed that sunlight does not completely bleach the ESR Al signal of quartz grains in aeolian sand from Australia (Tanaka et al. 1995) and in loess of northern Europe (Tissoux et al. 2010).

ESR Dating of Optically Bleached Marine Quartz Deposits

Tanaka et al. (1997) and Tissoux et al. (2008) applied ESR dating on known-age marine terrace sediments collected in Japan using Ti signal and Ti and Al signals, respectively. In both cases, it was apparent that the signal in the samples studied here had not received complete pre-burial bleaching. On the contrary, ESR dating of quartz from fossil beach in Nice, France (Falguères et al. 1988), and from fossil estuarine in the Somme Valley, France (Laurent et al. 1998), provided data in agreement with the expected ages. Burdette et al. (2013) showed that using the Ti–Li signal from sands from stranded ancient coastal deposits in Florida were in concordance with increasing geomorphic age and had ages older than OSL saturation indicated. Moreover, biostratigraphic age constraints in one sample were consistent with the ESR optical ages.

ESR Dating of Glacial Deposits

Together with sunlight bleaching, such grinding mechanisms could be an effective zeroing mechanism in ESR dating of glacially derived sediments. As such, the Ge-related impurity center in quartz was applied for the dating of Pleistocene glaciations in Central Asia (Zhou et al. 2002; Yi et al. 2002; Zhao et al. 2006, 2010). However, some fundamental points remain unclear as mentioned here above.

Summary or Conclusion

ESR applied on sedimentary quartz is a powerful dating method when applied on quartz extracted from fluvial, coastal, or desert or sediments deposited during the Plio-Pleistocene period.

Cross-References

- ▶ [Electron Spin Resonance \(ESR\) Dating - General Principles](#)
- ▶ [Electron Spin Resonance Spectrometer](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating of Coral](#)
- ▶ [Quartz](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Radiation Defect](#)
- ▶ [Radiation Dose Rate](#)
- ▶ [Teeth \(ESR/U-Series\) Electron](#)

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Rhenium–Osmium Geochronology: Sulfides, Shales, Oils, and Mantle

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Synonyms

Re–Os geochronology; ^{187}Re – ^{187}Os geochronology

Definition

Rhenium–osmium geochronology is based on radioactive decay of ^{187}Re to ^{187}Os with a half-life of 41.6 b.y. – about 10 times the age of the earth. Both Re and Os are siderophile-chalcophile elements, that is, they are both strongly partitioned into metals or sulfides rather than silicates. This distinguishes them from other widely used geochronometers whose parent-daughter elements reside in silicates. Re–Os geochronology underpins dating of materials from meteorites, the mantle, and metallic ore deposits. Furthermore, both Re and Os are redox-sensitive metals, soluble when oxidized, and fixed by reduction. Thus, both are mobile in Earth's presently oxidized surface environments but are concentrated in sulfides and organic matter in anoxic-euxinic sediments. This is the basis for Re–Os dating of the depositional age of organic-rich sedimentary rocks and provides a temporally constrained record of changing redox conditions through earth history.

Fundamentals of Re–Os Geochemistry

There are two naturally occurring isotopes of Re: stable ^{185}Re and radioactive ^{187}Re . Mass fractionation of the two Re isotopes is readily observed during the extreme conditions imposed by mass spectrometry (e.g., Suzuki et al. 2004; Zimmerman et al. 2007). The few reported natural variations, however, are less than 0.3 ‰ (Miller et al. 2009) and thus introduce errors less than other sources of uncertainty for Re–Os geochronology. As with other high-mass elements used in geochronology, we therefore assume uniform present-day abundances of ^{185}Re (37.398 %) and ^{187}Re (62.602 %; Gramlich et al. 1973) as an underpinning assumption for radiometric dating.

There are seven naturally occurring isotopes of Os: ^{184}Os , ^{186}Os , ^{187}Os , ^{188}Os , ^{189}Os , ^{190}Os , and ^{192}Os . Isotope ^{187}Os is the product of beta decay of ^{187}Re , with a decay constant of $1.666 \times 10^{-11} \text{ year}^{-1}$ (Smoliar et al. 1996). Isotope ^{186}Os is the product of alpha decay of ^{190}Pt with a decay constant of $1.542 \times 10^{-12} \text{ years}^{-1}$ (Walker et al. 1997). The abundances of the remaining isotopes may be considered constant for present-day Re–Os isotope geochemistry and geochronology. Prior to recognition of small, but measurable contributions of radiogenic ^{186}Os , Os isotopic compositions were reported as $^{187}\text{Os}/^{186}\text{Os}$. Current convention is to normalize abundances of ^{187}Os to ^{188}Os , reporting isotopic variations in terms of the ratio $^{187}\text{Os}/^{188}\text{Os}$.

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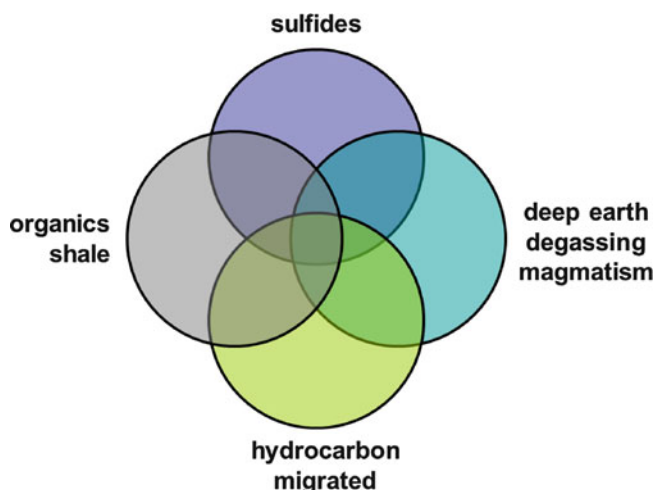


Fig. 1 Reservoirs important to the terrestrial Re–Os budget

Os is highly compatible in mantle sulfides and metal alloys and is thus strongly sequestered in the earth’s mantle relative to the crust. Re, in contrast, is only mildly compatible and is therefore transferred to the crust by partial melts far more efficiently than Os (e.g., Reisberg and Lorand 1995). Thus, $^{187}\text{Re}/^{188}\text{Os}$ ratios in fertile (undepleted) mantle are low (about 0.4), whereas $^{187}\text{Re}/^{188}\text{Os}$ ratios in the crust are much higher and extremely variable; crustal $^{187}\text{Re}/^{188}\text{Os}$ averages about 50 and ranges from one to three orders of magnitude (or more) higher than the mantle (Shirey and Walker 1998). The extreme variability in $^{187}\text{Re}/^{188}\text{Os}$ ratios offers two key opportunities. First, because $^{187}\text{Re}/^{188}\text{Os}$ ratios are markedly higher in the crust than in the mantle, decay of ^{187}Re over time produces an enormous range of $^{187}\text{Os}/^{188}\text{Os}$ ratios in crustal materials. This provides a sensitive tracer of crustal input to mantle or crustal contamination in mantle-derived materials. Second, extremely high $^{187}\text{Re}/^{188}\text{Os}$ ratios in some materials make them suitable for dating very young samples, despite the long half-life of ^{187}Re .

Figure 1 illustrates earth’s Re and Os reservoirs and Fig. 2 details the Re–Os budgets in various reservoirs, along with the potential for cycling among those reservoirs. Whereas subduction cycles crustal Re and Os into the mantle, partial melting and slab dehydration introduce the elements into the crust. The oceans receive Re and Os from seafloor hydrothermal processes, seafloor weathering, riverine inputs from continental weathering, rain of cosmic dust, and the occasional meteorite. Present-day input from continental weathering constitutes about 80 % of the Os budget of seawater (Sharma et al. 1997).

Fundamentals of Re–Os Dating: From Sample to Age

Analyses for high-precision Re–Os ages are acquired using the isotope dilution method, in which a known amount of one isotope of each element is added to the sample prior to analysis. Given the amount and composition of the isotopic “spike” added and the measurement of isotopic ratios in the mixture, it is straightforward to calculate the ratios in the sample. For example, the weight in μg of Re in a sample can be calculated as follows:

$$\text{Re}_w = \text{Spk}_w \frac{AW_{\text{sam}}}{AW_{\text{spk}}} \left[\frac{^{185}\text{Re}_{\text{spk}} - R_M^{187}\text{Re}_{\text{spk}}}{R_M^{187}\text{Re}_{\text{sam}} - ^{185}\text{Re}_{\text{sam}}} \right] \quad (1)$$

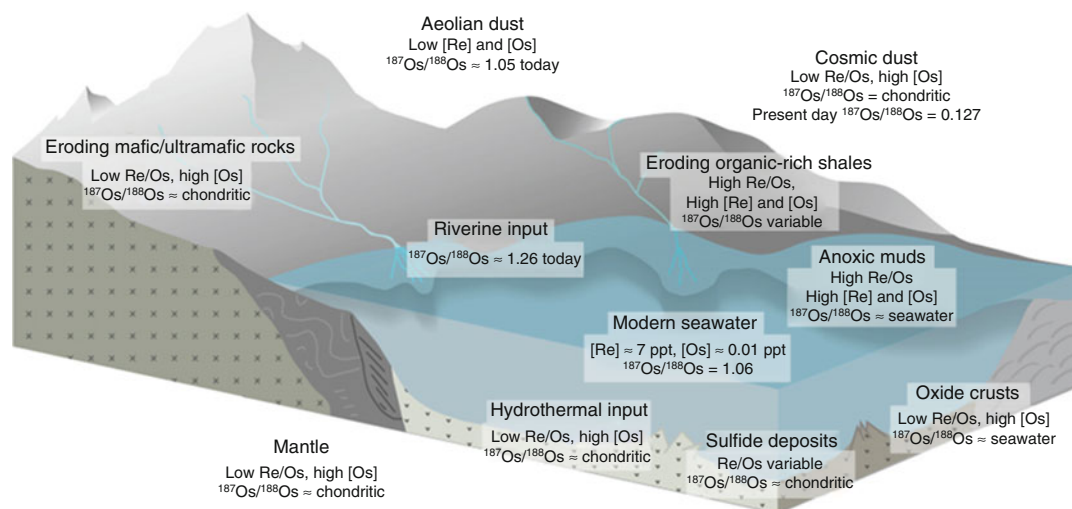


Fig. 2 Re and Os reservoirs with sources and sinks for seawater (From Hannah and Stein 2012). Riverine concentrations of Re and Os depend strongly on the composition of bedrock in the drainage area; flux to the oceans is a mixture of dissolved and suspended load. Therefore, global averages are not available. Data are summarized from a variety of sources, all cited in the main text

where Re_w = weight of Re in the sample, Spk_w = weight of Re in the spike (same units as sample), AW_{sam} = atomic weight of Re in the sample, AW_{spk} = atomic weight of Re in the spike, $^{187}Re_{spk}$ and $^{185}Re_{spk}$ = fraction of each isotope in the spike, $^{187}Re_{sam}$ and $^{185}Re_{sam}$ = fraction of each isotope in the sample, and R_M = measured $^{185}Re/^{187}Re$ ratio. Dividing Re_w by the weight of the sample in grams yields the concentration of Re in μg per gram, or ppm. Derivations, explanations, and examples of applications for this and many other calculations based on isotopic data are given in Faure and Mensing (2005).

Today, isotopic analyses of Re and Os are most commonly acquired in three steps: (1) dissolution of the sample and equilibration with isotopic spikes in a closed vessel; (2) chemical purification of Re and Os, separating each from the matrix and from each other; and (3) isotopic analysis of each element by negative thermal ionization mass spectrometry (NTIMS). For Step 1, the sample and spikes are loaded into thick-walled Pyrex tubes (Carius tube) with inverse aqua regia, sealed, and equilibrated for at least 24 h at 240 °C (Shirey and Walker 1995). To isolate organic matter or sulfides in shale samples without dissolving or significantly leaching detrital minerals, a solution of $CrO_3-H_2SO_4$ is used in place of inverse aqua regia (Selby and Creaser 2003; Kendall et al. 2004).

For Step 2, Os is separated from the solution in the Carius tube either by distillation (Morgan and Walker 1989) or dissolution in an organic phase (CCl_4 or $CHCl_3$) and back extraction into HBr (Shen et al. 1996; Cohen and Waters 1996; Brauns 2001), followed by microdistillation (Roy-Barman and Allègre 1995; Birck et al. 1997); both utilize the volatility of Os under oxidizing conditions and its quantitative drawdown into HBr. Re is subsequently purified on ion exchange columns (Morgan and Walker 1989).

For Step 3, although NTIMS is almost universally used for high-precision measurement of Os isotopes, some labs use solution multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to determine the Re isotopic ratio. Spot analyses, such as laser ablation MC-ICP-MS for Re–Os isotopic analyses, are not feasible in most cases for one or both of two reasons. First, most Os concentrations and some Re concentrations are too low, below detection limits for LA-MC-ICP-MS. Second, in some materials – notably in molybdenite – the radiogenic daughter isotope ^{187}Os may diffuse and collect in crystal defects, so that it is spatially decoupled from its parent ^{187}Re (Stein

et al. 2001, 2003; Košler et al. 2003; Selby and Creaser 2004). The resulting ages may be highly erroneous, either too old or too young (see discussion in later section).

Prior to interpretation of the isotopic data, raw measurements of isotopic ratios from mass spectrometry are corrected for instrumental mass fractionation, and all analytical uncertainties must be identified and appropriately calculated. Mass fractionation of Os isotopes is readily corrected for each measurement by using $^{190}\text{Os}/^{188}\text{Os} = 3.08271$ (Platzner 1999). Because Re has only two isotopes, however, and ^{185}Re is introduced as an isotopic spike, there is no stable, unchanging isotopic ratio in the sample to measure. If MC-ICP-MS is used, however, the sample can be doped with an element of similar atomic weight that has at least two stable isotopes, typically Ir or W, and the mass fractionation of those isotopes used to correct for that of ^{185}Re and ^{187}Re (e.g., Schoenberg et al. 2000; Li et al. 2010). For NTIMS, Re isotope fractionation is determined from repeated measurements of a standard and assumed to be the same for sample analyses. Measured ratios are corrected for mass fractionation and isobaric interferences. Other sources of uncertainty in Re–Os analyses arise from weighing, standard and spike calibrations, and blanks. The 2σ uncertainties for Re and Os abundances and the isotopic ratios are calculated by numerical propagation of all uncertainties.

Given the measured abundances of the parent (^{187}Re) and daughter (^{187}Os) isotopes, each normalized to ^{188}Os , a stable isotope, the age and initial composition of the Os can be calculated from the basic age equation:

$$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{measured}} = \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{initial}} + \left(\frac{^{187}\text{Re}}{^{188}\text{Os}}\right)_{\text{measured}} (e^{\lambda t} - 1) \quad (2)$$

where the measured ratios are determined from mass spectrometry, the initial ratio is the isotopic composition of Os at the time the sample equilibrated with and derived from its source, λ is the ^{187}Re decay constant, and t is the age of the sample in years. In any sample with measureable “common” Os (non-radiogenic Os incorporated into the sample when it formed), the initial Os isotopic composition of the common Os must be known. Thus there are two unknowns: the initial Os isotopic composition and the age. This is overcome by measuring multiple consanguineous samples and fitting a linear regression on an isochron diagram, a plot of the measured $^{187}\text{Re}/^{188}\text{Os}$ versus $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 3).

Some samples have very little or effectively no common Os on formation. The mineral molybdenite (MoS_2), for example, takes in large amounts of parent Re, but almost quantitatively excludes Os at the time of crystallization. Other sulfides may also have unusually high $^{187}\text{Re}/^{188}\text{Os}$ ratios in the thousands or tens of thousands – so-called low-level highly radiogenic (LLHR) samples (Stein et al. 2000). In such cases, for which the Os is nearly 100 % radiogenic, the traditional isochron diagram is meaningless. Any presumed measurement of ^{188}Os clearly carries an extreme uncertainty (since there is too little to measure!). This is described in more detail below in the sections that describe dating molybdenite and LLHR samples.

Historical Background

The promise of highly accurate and precise Re–Os chronology was realized in the mid-1990s after four major, analytical issues were overcome: (1) lack of sensitive mass spectrometry techniques, (2) poor stoichiometry of Os standard materials, (3) difficulty equilibrating spike and sample Re and Os, and (4) uncertainty in the ^{187}Re decay constant. Resolving these issues opened the door to a wide

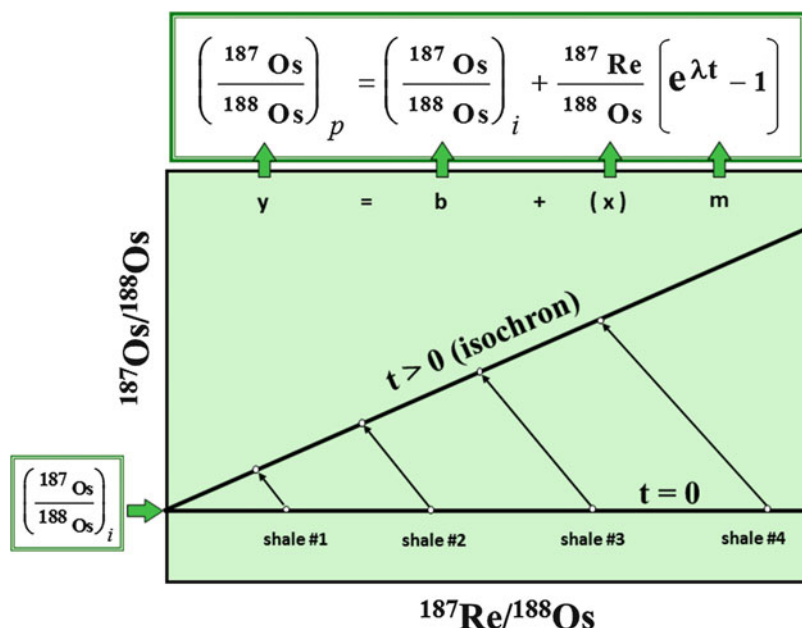


Fig. 3 Example of a Re–Os isochron plot. Four shale samples (or four related sulfide minerals), for example, were deposited at time zero, and all acquired Os from seawater with the same initial $^{187}\text{Os}/^{188}\text{Os}$ ratio. Over time, as ^{187}Re decays to ^{187}Os , the position of each point shifts up and to the right. The increase in $^{187}\text{Os}/^{188}\text{Os}$ is proportional to the magnitude of $^{187}\text{Re}/^{188}\text{Os}$ for each point. Linear regression of the four points at $t > 0$ yields a straight line with the equation shown. The slope ($m = e^{\lambda t} - 1$) is a function of the age of the sample and the decay constant. The y-intercept is the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio, the ratio that would exist in a sample that had no parent ^{187}Re . The uncertainties on the slope and initial $^{187}\text{Os}/^{188}\text{Os}$ ratio depend on the analytical uncertainties for each data point and the goodness of fit (MSWDs, or mean square of weighted deviations) for the regression

range of applications for geologic problems from the mantle to the crust, from magmatic systems to surface processes.

Negative TIMS

Many isotopic methods rely on measurements of positive ions by thermal ionization mass spectrometry (TIMS). Recognition that both Re and Os are much more efficiently ionized as negative ions enabled far more precise measurements of Re and Os isotopic compositions on picogram quantities (Creaser et al. 1991; Völkening et al. 1991). The switch to negative TIMS (NTIMS) was critical to the development of Re–Os isotope geochemistry of crustal materials, as many labs turned to this new and more precise analytical tool. Analysis of Re isotopes by MC-ICP-MS has continued in some labs because it affords the opportunity to correct for instrumental mass fractionation of Re isotopes. In addition, a few labs have developed high-precision methods for analysis of Os isotopes by direct sparging of Os from the reaction vessel into an MC-ICP-MS (e.g., Hassler et al. 2000; Nozaki et al. 2012; Sen and Peucker-Ehrenbrink 2014).

Stoichiometry of Os Standards

Accurate concentration analyses using isotope dilution depend critically on the accuracy of the gravimetric standards used to calibrate spikes. The materials used to make Os standards are notoriously nonstoichiometric, leading to inherent errors in the calculated Os concentrations (Morgan et al. 1995). Alternative materials have been used to overcome this (Shen et al. 1996; Yin et al. 2001), but the inconsistencies remained. Selby and Creaser (2001) adapted an earlier method (Gilchrist 1932) to reduce ammonium hexachloroosmate to a pure osmium metal sponge

and thereby directly measure the Os content of the salt. A further adaptation of this method yields a robust measurement for the Os standard used today at AIRIE (Markey et al. 2007). Nevertheless, the persistent problem with stoichiometry of Os gravimetric standards remains challenging.

Spike Challenges: Equilibration Difficulties and the Mixed Re-double Os Spike

A long-standing challenge was achieving isotopic equilibrium between the sample and Os spike without loss of Os. Loss of Os is especially problematic for open-vessel methods or use of PTFE vessels, through which Os may diffuse. External precision (reproducibility) was greatly improved as laboratory methods moved from less reliable equilibration of spike and sample Re and Os by oxidizing alkaline fusion (Morgan and Walker 1989; Markey et al. 1998) to high-pressure and high-temperature sample dissolution and spike equilibration using inverse aqua regia in a sealed Carius tube (Shirey and Walker 1995).

A particular challenge with spiking is presented by samples with low concentrations of common Os and very high concentrations of radiogenic ^{187}Os . There are no well-measured ratios of Os isotopes that are neither radiogenic nor impacted by the addition of the spike. Thus, there is no mechanism for monitoring mass fractionation or determining the amount of common Os. These problems were resolved simultaneously with development of a mixed Re-double Os spike (^{185}Re – ^{188}Os – ^{190}Os ; Markey et al. 2003). Sufficient ^{188}Os spike is added to match the abundance of ^{187}Os , so that the $^{187}\text{Os}/^{188}\text{Os}$ ratio is well measured. In the same spike solution, a small amount of ^{190}Os is used to achieve a well-measured ratio with ^{192}Os , the most abundant isotope in the common Os spectrum. The well-determined $^{188}\text{Os}/^{190}\text{Os}$ ratio is used for the fractionation correction, while the balanced $^{190}\text{Os}/^{192}\text{Os}$ ratio is used to determine the amount of common Os in the sample. At the same time, use of a mixed Re–Os spike eliminates weighing errors associated with spike addition. This breakthrough has dramatically improved the precision and accuracy of Re–Os ages for young molybdenites and LLHR samples.

Half-Life Hurdles: The ^{187}Re Decay Constant

Establishing the half-life of a parent isotope with certainty is imperative for radiometric dating. Molybdenite, with its extraordinarily high Re concentrations and negligible common Os, contains essentially pure ^{187}Os , thereby providing the first reliable estimates of the half-life of ^{187}Re at about 43.5 b.y. (Herr and Merz 1955; Hirt et al. 1963).

Fifteen years later, the ^{187}Re half-life was determined at 45.6 ± 1.2 b.y. by assuming the slope of a meteorite isochron represented an age of 4.550 Ga (Luck and Allègre 1982). Re–Os ages for 11 molybdenites based on this revised half-life showed that, in a few cases, ages were too old (some older than the age of the earth). These highly inaccurate results were attributed to Re loss due to metamorphic and/or hydrothermal processes (Luck and Allègre 1982) – a major setback for Re–Os dating of molybdenite, as the chronometer was labeled as unreliable.

The half-life of ^{187}Re was again redetermined as 42.3 ± 1.3 Ga by measuring ingrowth of ^{187}Os over several years in a purified kilogram of Re (as perhenic acid, HReO_4 ; Lindner et al. 1989). Analysis of the same molybdenites that previously gave aberrant ages (Luck and Allègre 1982) now produced ages in good agreement with wall rock ages determined by other isotopic methods, leading to the conclusion that earlier discordant results reflected sample-spike equilibration problems rather than issues with the molybdenite chronometer (Suzuki et al. 1992, 1993).

The 3 % uncertainty on the ^{187}Re half-life determined by Lindner et al. (1989) placed serious limits on Re–Os geochronology. Two labs simultaneously undertook improvements by back-calculating the ^{187}Re decay constant from Re–Os isotope systematics in iron meteorites well dated by other methods. Shen et al. (1996) calculated a ^{187}Re decay constant of $1.66 \times 10^{-11} \text{ year}^{-1}$; while

they do not report an uncertainty for their decay constant, it is tied to the 1.2 % uncertainty on the calibration of their Os tracer. Smoliar et al. (1996) examined Re–Os systematics in group IIIA iron meteorites; by assuming these formed at the same time as angrite meteorites that yield a concordant Pb–Pb model age (Lugmair and Galer 1992), they were able to calculate the ^{187}Re decay constant at $(1.666 \pm 0.017) \times 10^{-11} \text{ year}^{-1}$. The assumption that the analyzed group IIIA and angrite meteorites are the same age is supported by agreement within $\pm 5 \text{ m.y.}$ of the ^{53}Mn – ^{53}Cr formation intervals. The $\pm 1.02 \%$ uncertainty calculated for the Smoliar et al. (1996) ^{187}Re decay constant can be reduced to $\pm 0.31 \%$ if the lab's Os standard can be tied back to the University of Maryland standard used by Smoliar et al. (1996).

Persistent Misperceptions

It is not about closure temperatures! Rather, it is the “container” that assures isotopic closure. The geochemical behavior of Re and Os controls the reliability of the Re–Os chronometers. Neither element is accommodated by silicate minerals, and neither element is soluble in reducing aqueous fluids. Thus, there are only two routes for either Re or Os to escape from its hosting phase: (1) sit adjacent to another phase with a comparable affinity for either Re or Os under conditions that allow diffusion or (2) interact with an oxidizing fluid. An isolated sulfide mineral surrounded by silicates will not lose Re or Os. Surface weathering or attack by any oxidizing fluid, in contrast, promotes disturbance of the Re–Os isotopic system (e.g., Georgiev et al. 2012).

A “Model 1” isochron does not mean “precise and accurate”! Many labs plot isochrons from their data using the freely available software Isoplot (Ludwig 2012). The first model for linear regression used by Isoplot is termed “Model 1” and assumes that scatter of data from the straight line is attributable only to the uncertainties of the individual data points (following York 1969). The program also calculates a “probability of fit” and rejects the Model 1 regression if the probability is $< 15 \%$. (The user may change this value to any probability between 5 % and 30 %.) If the Model 1 regression is rejected, Isoplot calculates a “Model 3” age, which assumes an unknown, but normally distributed variation in the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio. This change in regression model results in a larger age uncertainty. In fact, the size of the uncertainties for individual data points strongly impacts the choice of model – the larger the uncertainties, the higher the probability of fit, and therefore, the greater likelihood that the Model 1 fit will be accepted. Thus, “better” data – that is, more precise analyses and/or underestimated analytical uncertainties – are less likely to result in a Model 1 regression. Conversely, less precise measurements and/or overestimated analytical uncertainties for each data point readily result in an unwarranted Model 1 regression. Examples of improbably high analytical uncertainties and overly optimistic isochrons are all too common.

A lower MSWD does not always mean a better isochron! Ludwig (2012, footnote on p. 22) eloquently states the meaning of “MSWD”:

MSWD = Mean Square of Weighted Deviates. This does not refer to porcine pervers; it is, roughly, a measure of the ratio of the *observed* scatter of the points (from the best-fit line) to the *expected* scatter (from the assigned errors and error correlations). *The MSWD parameter cannot be compared to the classical R^2 parameter, and is not a measure of how highly correlated the X- and Y-values are.* If the assigned errors are the only cause of scatter, the MSWD will tend to be near unity. MSWD values much greater than unity generally indicate either underestimated analytical errors, or the presence of non-analytical scatter. MSWD values much less than unity generally indicate either overestimated analytical errors or unrecognized error-correlations.

In short, a low MSWD may result from an overestimation of analytical uncertainties. Equally important, an $\text{MSWD} \ll 1$ suggests that analytical uncertainties have been underestimated – though it can also indicate an extraordinarily colinear data set. Ideally, for a precise isochron based on good measurements of well-behaved samples, the MSWD will be close to 1.

Applications

The many improvements made during the 1990s for analytical methods and standards opened a world of new applications for Re–Os geochronology. Precision and accuracy of measurements of meteoritic material and mantle xenoliths greatly increased. With the Smoliar et al. (1996) ^{187}Re decay constant, the first NTIMS analyses of molybdenites aligned with U–Pb ages for related zircons (Stein et al. 1997, 2001). High-precision and accurate analyses of low-level basalts, crustal sulfides, and organic matter became a reality. The next sections provide an overview of these applications, each of which is also discussed in separate focused and condensed chapters in this volume. Here we pay particular tribute to the development and application of the Re–Os molybdenite chronometer, as its value is no less than that of zircon dating.

Meteorites and Mantle

Much of the early work on Re–Os systematics in earth materials focused on xenoliths from the earth's mantle and on meteorites (see also entry “► [Meteorites \(Re–Os\)](#)”). Prior to the 1990s, analytical limitations required the use of materials with relatively high concentrations of Re and Os. More importantly, the strong fractionation of both Re between earth's mantle and mantle-derived partial melts, and of both Re and Os between silicates and metals, affords ample opportunities to explore the origins of planetary bodies and the evolution of planetary interiors. Re–Os systematics can reveal the age and probable origin of meteorites from the solar nebula, the formation of Fe–Ni cores, and timing of secondary alteration (cf. Walker, this volume). Studies focused on shergottite meteorites, of Martian origin, reveal the evolution of the Martian mantle, early magma ocean, and late accretion (e.g., Brandon et al. 2012).

Re–Os isotopic studies of mantle xenoliths, exposed mantle peridotites, and mantle-derived basalts provide high-quality information on melt-depletion events in the mantle, the evolution of the mantle through time, and the preservation of subcontinental mantle lithosphere. Reisberg et al. (2004) provide an example of multiple processes impacting Os isotope composition of mantle samples preserved as xenoliths, deriving useful model ages for melt extraction, yet questioning the interpretation of these data as mantle stabilization ages. Rudnick and Walker (2009) give an excellent review of the fundamentals, potential pitfalls, and lessons learned in two decades of Re–Os applications in the mantle.

Crustal Sulfides

Molybdenite Geochronology

Molybdenum disulfide (MoS_2) or molybdenite is a silver-colored mineral with a distinct bluish tint. The blue tint is particularly notable in samples with high Re. This hexagonal (rarely trigonal) mineral is soft, has a distinct platy cleavage, and can easily be bent with the fingers (Fig. 4). Molybdenite occupies a unique niche – it is the only naturally occurring mineral that takes in significant Re, usually at the level of tens to hundreds of ppm, other than its exceedingly rare Re-rich solid-solution cousin, rehiite (ReS_2 ; Korzhinsky et al. 2004; Tessalina et al. 2008). Molybdenite occurs in a wide range of geologic environments. Almost invariably, it is present in porphyry-style ore deposits worldwide. It may also be found as a minor accessory mineral in silicic-felsic metamorphic rocks and biotite gneisses. Molybdenite is most commonly associated with quartz veins or as disseminated blades or rosettes in felsic magmatic-metamorphic rocks (Fig. 5). The ability to directly date molybdenite gave the economic geology community accurate and precise ages for a wide array of ore deposits and gave the geologic community direct ages for sulfide occurrences in the earth's crust (Stein et al. 2001; cf. review in Stein 2014).

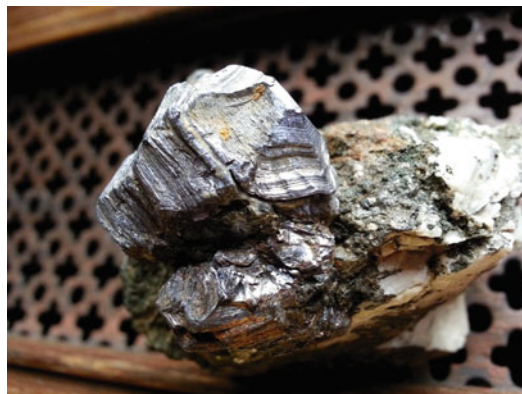


Fig. 4 Molybdenite crystals from Råde, Norway, illustrate hexagonal form and platy texture. This exceptional specimen is about 6 cm across and belongs to the Natural History Museum in Oslo. Crystals as large as 15 cm in diameter have been reported from Råde (Photo by H. Stein)

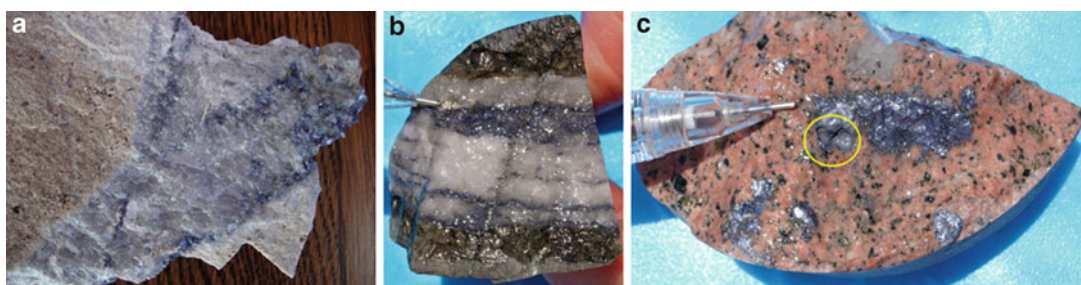


Fig. 5 (a) Quartz-molybdenite veins in the Primos rhyolite porphyry, Henderson Mo porphyry deposit, Colorado. Field of view is 10 cm across. (b) Banded quartz-molybdenite vein cutting fine-grained biotite hornfels, Myszków Mo deposit, Poland. Thumb and forefinger to right, pencil tip to left for scale. Sample is wet to enhance contrast. (c) Porphyritic granite with disseminated molybdenite and minor finely disseminated chalcopyrite (*bottom center*) from the Myszków Mo deposit, Poland. Two drill pits (*inside yellow circle*) show how molybdenite is excavated for Re–Os dating. Pencil tip for scale. Sample is wet to enhance contrast (Photos by H. Stein)

Uniquely, molybdenite has very high Re/Os ratios on crystallization (generally $>10^6$) and takes in essentially no common (i.e., initial) Os. If common Os is present in the sulfide-depositing fluid, it is accommodated by other co-crystallizing sulfides. With vanishingly low common Os (and therefore, no initial ^{187}Os) in molybdenite, the decay equation for calculating a molybdenite age is elegant in its simplicity:

$$^{187}\text{Os}_{\text{measured}} = ^{187}\text{Os}_{\text{initial}} + ^{187}\text{Re}_{\text{measured}}(e^{\lambda t} - 1) \quad (3)$$

reduces to

$$^{187}\text{Os}_{\text{measured}} = ^{187}\text{Re}_{\text{measured}}(e^{\lambda t} - 1) \quad (4)$$

Here the model age (t), reflecting the time of crystallization, is the only unknown. The age is therefore readily determined from a single sample of molybdenite. Lambda (λ) is the ^{187}Re decay constant.

The ^{187}Re – ^{187}Os radiometric clock held in the mineral molybdenite was explored in earnest in the 1960s (Hirt et al. 1963; Herr et al. 1967). Analytical issues and a poorly determined ^{187}Re decay

constant stalled progress. In the 1990s, early pioneering work in ^{187}Re – ^{187}Os dating of molybdenite was carried out by Du Andao, a Chinese chemist, who early on realized the potential of the method for this mineral (Du et al. 1995). Her lab quickly became a venue for many Chinese geologists to simply acquire dates from her for Chinese ore deposits, and a hailstorm of papers reporting molybdenite ages ensued. These geologists depended on her meticulous work and laboratory results. Also in the 1990s, another chemist, Katsuhiko Suzuki, was independently exploring molybdenite as a geochronometer in Japan. His lab became a focal point for mixing geologists and geochemists to jointly tackle geologic problems with Re–Os isotope geochemistry. In the early 1990s, both Drs. Du and Suzuki were limited by the analytical capability offered by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) prior to the advent of multi-collector instruments.

Other groups were also limited by ICP-MS instrumentation and by assessing the accuracy of ^{187}Re – ^{187}Os molybdenite ages through their agreement with K–Ar ages (e.g., McCandless and Ruiz 1993). It soon became clear that primary ages in the ore-forming environment were held by molybdenite and not by traditionally dated ore-associated gangue minerals (e.g., alunite and sericite), for which argon-based dating had been employed (Suzuki et al. 1996; Watanabe and Stein 2000; Stein et al. 2001; Selby et al. 2002).

The ages achieved by early workers, nonetheless, were encouraging. But a breakthrough in analytical technology was needed. This was delivered with NTIMS (Negative Thermal Ionization Mass Spectrometry), as two working groups realized that Re and Os could be measured as negative ions (Creaser et al. 1991; Völkening et al. 1991). This analytical breakthrough was immediately utilized to successfully develop the ^{187}Re – ^{187}Os chronometer in molybdenite, achieving accurate ages at high precision (Stein et al. 1997; Markey et al. 1998).

In addition to analytical challenges, a limiting factor in putting the molybdenite chronometer to use was the accurate determination of the ^{187}Re decay constant and its uncertainty. Ultimately, the ^{187}Re decay constant of Smoliar et al. (1996) became the established value and is the most widely used today. More recent attempts to further revise the ^{187}Re decay constant by pairing up molybdenite Re–Os and zircon U–Pb ages from the literature (Selby et al. 2007a) rely on two geologic assumptions: (1) molybdenite and zircon formation are contemporaneous, and implicit to the first assumption, (2) there is only one generation of molybdenite and one episode of zircon formation at a locality. In hindsight, geologic reason tells us this assumption is flawed; when multiple dates are available, molybdenite (and zircon) generally shows a range of ages at a single locality. The cleanest data sets are from porphyry-style deposits, but these also may have extended durations (e.g., Los Pelambres, Chile; Stein 2014). Therefore, the ^{187}Re decay constant that ties back to the meteorite community is best used; the complexities of crustal rocks do not lend themselves well to establishing decay constants.

Still other vexing issues lay ahead before ^{187}Re – ^{187}Os dating of molybdenite would become mainstream geochronology. Recognition of parent-daughter (^{187}Re – ^{187}Os) decoupling within molybdenite crystals presented a new challenge (Stein et al. 2001). Qualitative trial-and-error studies with different grain sizes, different crystals (chopped with a razor, peeled along cleavage planes, or powdered by drilling), different occurrences, and different milligram quantities of molybdenite revealed that geologic sense, not quantity, of molybdenite should drive the sampling. If part of a crystal is sampled, then the whole crystal must be sampled to ensure that all of the parent and daughter are included in the analysis. In fact, acquisition of the molybdenite mineral separate in a geologically meaningful context is the most critical step for molybdenite dating (Stein et al. 2001; Stein 2006, 2014). Unlike the approach for zircon U–Pb dating, whole-rock crushing to acquire a vial of molybdenite grains puts Re–Os dating at risk. If more than one generation of molybdenite is present, even if closely spaced in time, this approach yields variable ages that cannot be well

reproduced. In the same way, if decoupling is present at the scale of the sampling, ages will be variable and cannot be well reproduced. *It is the inability to replicate an age from the same separate that signals decoupling.* The decoupling of ^{187}Re – ^{187}Os in molybdenite is generally greater in coarser-grained samples, in older high-Re molybdenites that have accumulated significant radiogenic ^{187}Os , and in deformed molybdenites (Stein et al. 2003). Simply put, the accumulated radiogenic Os is desperate to get comfortable in the molybdenite structure and, at any opportunity, will migrate to crystal defects or dislocations (Stein et al. 2003). The early empirical recognition of parent-daughter decoupling was later verified through LA-ICP-MS of molybdenite (Stein et al. 2003; Selby and Creaser 2004). Thus, laser ablation technology cannot be used for ^{187}Re – ^{187}Os molybdenite dating (e.g., Košler et al. 2003). A subsequent atomic level study confirmed the suspected mobility of radiogenic Os within the molybdenite structure (Takahashi et al. 2007).

A unique aspect of ^{187}Re – ^{187}Os dating of molybdenite is that this sulfide rarely forms overgrowths (Stein et al. 2004; Aleinikoff et al. 2012). This is not the case for other sulfides; for example, pyrite is notorious for overgrowths. Without the complexity of overgrowths, this makes working with molybdenite far simpler than deciphering some U–Pb histories in zircon and monazite. Another positive feature is that the molybdenite chronometer remains intact, even at granulite facies temperatures (e.g., Bingen and Stein 2003). Compromise of the ^{187}Re – ^{187}Os clock in molybdenite should not be associated with temperature, but with chemical stability of sulfide (i.e., oxidation; cf. discussion in Stein 2014).

In nature, however, there are always exceptions when things at first seem simple. Though rare, a small population of molybdenites began to show up with measurable common Os. Not surprisingly, these molybdenites generally occur in the absence of other sulfides that accommodate Os, a platinum group element (PGE), in their structures. Silicate minerals typically do not substitute Os in their structures, so in such circumstances this left molybdenite vulnerable to squeezing Os into its structure. This reality led to the development of a mixed Re-double Os spike, now widely in use, for analyzing molybdenite (Markey et al. 2003). The concept is simple: a single spike solution contains enriched ^{185}Re – ^{188}Os – ^{190}Os . The ^{185}Re is used to determine the parent ^{187}Re concentration in a molybdenite sample, as there are only two isotopes of Re. The ^{188}Os in the spike solution is used to precisely determine the radiogenic ^{187}Os , just one amu (atomic mass unit) away, and the ^{190}Os is used to determine the ^{192}Os (the most abundant common Os mass). From these measurements, the total Re and Os concentrations in the sample can be reconstructed, and the dating is atomically accurate. Further, the double Os spike eliminates weighing errors for single Re and Os spike solutions and permits a mass fractionation correction for Os (Markey et al. 2003).

A new technology requires a reference material that can be accessed by multiple labs and used for interlaboratory comparison. Early workers used a well-homogenized, milled molybdenite powder from the Huanglongpu Mo deposit in China to assess internal (within lab) and external (between labs) repeatability of age results (Stein et al. 1997; Selby and Creaser 2001; Du et al. 2004). From this, the concept of a molybdenite isochron was derived, with the regression line defined by coupled variation in ^{187}Re and ^{187}Os concentrations and projecting to an intercept of zero initial ^{187}Os (Stein et al. 1997). Subsequently, a milled molybdenite powder from the Henderson mine in Colorado was characterized as a reference material (Markey et al. 2007). Molybdenite from this particular porphyry Mo deposit was specifically chosen for three reasons: (1) undeformed, minimizing decoupling issues, (2) relatively low Re, and (3) young age (27.656 ± 0.022 Ma), limiting the amount of ^{187}Os introduced as a possible lab contaminant. The Henderson molybdenite was endorsed by NIST (RM#8599) and can be purchased through NIST as a reference material for ^{187}Re – ^{187}Os age determinations. Importantly, RM#8599 is not a reference material for Re and ^{187}Os

concentrations, only for the accuracy of ^{187}Re – ^{187}Os ages. The Re and ^{187}Os concentrations vary, but are perfectly coupled such that the age is highly reproducible (Markey et al. 2007).

While dating ore deposits was the original motivation and a primary application for molybdenite dating, the mineral's widespread occurrence as an accessory phase provides additional opportunities. Molybdenite crystallization can be tied to specific tectonic events, yielding timing, for example, of fluid-flow events during metamorphism (Stein 2006), specific deformation events (Stein and Bingen 2002), and progressive and episodic extensional tectonism (Zimmerman et al. 2008).

In sum, molybdenite presents the geologic community with a simple, yet elegant, radiometric clock through ^{187}Re – ^{187}Os . What was novel turned mainstream with NTIMS, the use of a double Os spike, and a certified reference material for the community. Depending on Re concentration in the molybdenite, the chronometer can accommodate samples from Early Archean to well less than 1 Ma. Potential decoupling can be overcome with sensible sampling and thoughtful mineral separation. For a detailed review of molybdenite and sulfide geochronology, rich in examples, consult Stein (2014).

In this brief section, we have focused on the steps leading to breakthroughs and the hurdles in establishing the ^{187}Re – ^{187}Os chronometer for this unassuming, soft, pliable, and isotopically strong mineral.

LLHR (Low-Level Highly Radiogenic) Sulfides

The LLHR term was introduced to describe samples with molybdenite-like Os isotopic compositions but with much lower Re concentrations, at the ppb or even ppt level (Stein et al. 2000). That is, the common Os is low enough relative to the radiogenic ^{187}Os that single samples may provide accurate and precise ^{187}Re – ^{187}Os ages. The principles are the same as described for molybdenite, with the caveat that the blank correction may be important. The key equation for dating is therefore Eq. 4 (above).

Arsenopyrite (FeAsS) and some pyrites (FeS_2) may be LLHR. Because arsenopyrite and pyrite are commonly associated with Au, these two sulfides are sought out for dating gold deposits when molybdenite is absent from the sulfide assemblage. Like molybdenite, arsenopyrite and pyrite may permit ^{187}Re – ^{187}Os dating of ore deposits. Further, pyrite is the most common sulfide in the earth's crust, so this mineral has additional value for Re–Os geochronology in general. If sulfides, including arsenopyrite and pyrite, have significant common Os, they can still be dated using the traditional $^{187}\text{Re}/^{188}\text{Os}$ versus $^{187}\text{Os}/^{188}\text{Os}$ isochron approach, but this requires analyses of multiple contemporaneously formed samples. For further discussion of LLHR samples, refer to Stein (2014). Several key studies brought attention to arsenopyrite as a valuable sulfide for Re–Os dating (Arne et al. 2001; Bierlein et al. 2006; Morelli et al. 2005, 2007, 2010). In addition, Morelli et al. (2010) showed that the Re–Os systematics in arsenopyrite were intact, even at temperature $>400^\circ\text{C}$. Although unusual, even pyrrhotite can be LLHR, yielding primary ages if the sample does not include other sulfides (Demaiffe et al. 2013).

Dating Shales: Source Rocks for Oil

The Re–Os budget held in crustal rocks is dominated by shales (Fig. 1). Groundbreaking Re–Os work on dating shales relied on whole-rock analyses of organic-rich shales (e.g., Ravizza and Turekian 1989; Creaser et al. 2002). Subsequently, Hannah et al. (2004) made use of syn-sedimentary pyrite with remarkable success on samples of Paleoproterozoic age ($2,316 \pm 7$ Ma). The field of Re–Os geochronology quickly expanded to include dating of the organic (hydrogenous) component of organic-rich shales isolated from the clastic or detrital component of the shale (e.g., Selby and Creaser 2003, 2005a; Kendall et al. 2009; Yang et al. 2009). Re and Os concentrations in the organic

component are easily in the ppb range. The technique soon became well established as a tool to place age pins in the stratigraphic column for geologic time scale calibration. Previously, only U–Pb zircon ages on ash beds had prevailed as absolute time markers in sedimentary sections. Absolute time is also a valuable commodity for correlations where provincial species could not be used to link widely separated paleogeographic terranes (e.g., Xu et al. 2009).

The newfound ability to date shales led quickly to dating key units associated with major earth events; this can help resolve debates over the reach of these events in time and space – whether global or regional, abrupt or protracted. For example, localities with shale records associated with Neoproterozoic glaciation and the theory of a frozen snowball earth could now be time-bracketed with Re–Os dating of shales (e.g., Kendall et al. 2004, 2006, 2013; Rooney et al. 2010, 2011). Other earth events such as biotic crises associated with mass extinctions or major faunal turnovers provide excellent venues for Re–Os dating, as widespread anoxia preserved vast areas of organic material intact with their trace metal record of toxic seawater (e.g., Turgeon and Creaser 2008; Selby et al. 2009; Georgiev et al. 2011; Xu et al. 2014).

Since organic-rich black shales are potential source rocks for hydrocarbons, the petroleum industry became immediately interested in using the method not only as a measure of absolute time but as a correlation tool across basins, continents, and hemispheres. Good isochron regressions define initial $^{187}\text{Os}/^{188}\text{Os}$ ratios for paleo-seawater, useful measures for what was entering, mixing with, and characterizing the Re–Os budget of oceans on a more global scale (see Fig. 8). Simplistically summarized, the marine geochemical record, including Re–Os chemistry, is transferred to black shales on the seabed. During periods in earth history when the whole of seawater may have been anoxic, including the photic zone (e.g., Grice et al. 2005), the connection between top and bottom is profound. A more stratified ocean with variable oxygenation presents a more complex architecture linking the photic zone and seabed. This scenario holds for anoxic-euxinic waters in lacustrine sediments as well. With adequate ventilation and mixing, the seawater (lake water) Os isotope ratio represents the balance of (1) continental erosion (intimately linked to continental uplift) and (2) hydrothermal input. *Continental erosion* at a particular time in earth history reflects the kinds of rocks that are dominating the erosional cycle, that is, what rivers are delivering to seas. *Hydrothermal input* at a particular time in earth history may be dominated by mafic magmatism penetrating the seabed or terrestrial volcanic systems belching aerosols and particulate matter that ultimately mix at the seawater interface where they may incite algal blooms or otherwise feed microorganisms in the photic zone. While the notion of a global seawater Os isotopic composition is a tidy concept, it soon became apparent that restricted basins and isolated water masses, both horizontally and vertically, both locally and widespread, have the potential to harbor Os isotopic compositions that deviate from an assigned global Os isotopic value. Nevertheless, the concept of a variable Os isotopic composition for seawater through time works well, and the short residency time for Os in seawater gives us an increasingly tuned record of past earth events at high resolution (see Fig. 8).

As discussed throughout this contribution, the Re–Os data are governed by geologically responsible sampling. Drill core samples are highly preferred to outcrop samples to eliminate the possibility of disturbed isotope systematics related to weathering (Georgiev et al. 2012). At a minimum, flawed sampling at the outset compromises results and, more seriously, may disguise potentially meaningful results. Since we do not know the rate of sedimentation, proper sampling of shale means that the smallest possible interval, *but representative*, should be taken. After this interval is powdered, an aliquot of several hundred milligrams is removed for the Re–Os analysis. Sampling too large a stratigraphic interval risks capturing too large an interval of time – this compromises isochroneity and risks reducing the spread of the data points for a statistically well-constrained

isochron regression. Sampling too small a stratigraphic interval risks capture of postdepositional, small-scale isotopic exchange – for example, exchange among organic particles and sulfides after pore waters have been isolated from the overlying water column or redistribution of sediment by burrowing organisms.

What does this mean for Re–Os shale chronology? First, there is no threshold value for the amount of shale to be acquired, pulverized, and homogenized; each interval of core requires its own sampling strategy. Ideally, an isochron is derived from 5 to 8 samples, taken from 20 to 30 cm of core (Fig. 6). Sampling for an isochron should not be carried out over many meters or tens of meters of section. *Generally* speaking, for 20–30 stratigraphic centimeters of section and for ideal, well-laminated black shales without bioturbation, <30 g of pulverized shale sample (i.e., <1 cm stratigraphic span) routinely provides good ages (Fig. 7 and discussion in caption). Again, these are *generalized* parameters, and the sample stratagem depends on depositional rates, stability of the initial Os ratio, and Re/Os ratios in the shale samples. Shales with lower Re require larger aliquots for the analyses, but not necessarily larger bites of the stratigraphic section for homogenization.

Os Isotope Seawater Curve

The Os isotopic composition of the oceans has varied through time because of changes in the balance among the various Os sources, especially inputs from continental weathering (e.g., Peucker-Ehrenbrink and Ravizza 2000) and the several mechanisms for acquiring chondritic Os. Organic-rich sedimentary rocks, especially black shales, hold a record of ancient seawater Os isotopic composition. By far the best evidence that a sedimentary section has remained closed to Os gain, loss, or isotopic exchange is a suite of samples that form a precise isochron. In the last two decades, since high-precision Re–Os geochronology became a reality, a growing archive of initial $^{187}\text{Os}/^{188}\text{Os}$ ratios and corresponding ages has been acquired from isochrons. Figure 8 shows a plot of seawater $^{187}\text{Os}/^{188}\text{Os}$ versus age; for comparison, the Sr isotope seawater curve (Howarth and McArthur 1997; McArthur et al. 2001; Shields 2007) is plotted on the same figure. The well-known Sr isotope curve reflects four decades of effort; the Os isotope curve is in its early stages, with much still to be developed. In addition to these data, a number of studies have generated calculated initial $^{187}\text{Os}/^{188}\text{Os}$ ratios, derived from Re–Os isotopic ratios and a known (or assumed) age (e.g., Peucker-Ehrenbrink et al. 1995). Although a closed isotopic system is not proven, many of these data are likely valid, especially for young samples, and the effect of outliers tends to be swamped by the sheer volume of data. Studies based solely on calculated initial $^{187}\text{Os}/^{188}\text{Os}$ ratios have effectively illustrated, for example, the effect of a bolide impact at the Cretaceous-Paleogene boundary (Peucker-Ehrenbrink et al. 1995).

Figure 8 reveals a striking difference between the Sr and Os isotope seawater curves: the Os curve is spiky, with sharp highs and lows; the Sr curve is smooth, with more subdued variations. This is a simple result of the relatively long residence time for Sr in the oceans (~2 m.y.; McArthur et al. 2000) and the comparatively short residence time for Os (~28,000 years, Georg et al. 2013; still controversial, Paquay and Ravizza 2012). Short-term effects, such as bolide impacts or inputs from large igneous provinces, readily deflect the Os curve but are washed out by the long residence and mixing of Sr isotopes in seawater. A second critical difference is the continual buildup of Re and thus radiogenic Os in the crust. Neither element was mobilized in surface environments under earth's anoxic Archean atmosphere (Hannah et al. 2004), but both have accumulated since then, sequestered in large amounts in organic-rich sedimentary rocks. While both the Sr and Os seawater curves reflect variable input from continental weathering, Os is strongly controlled by the proportion of organic-rich sedimentary rocks undergoing weathering (Georgiev et al. 2012), whereas the Sr isotope

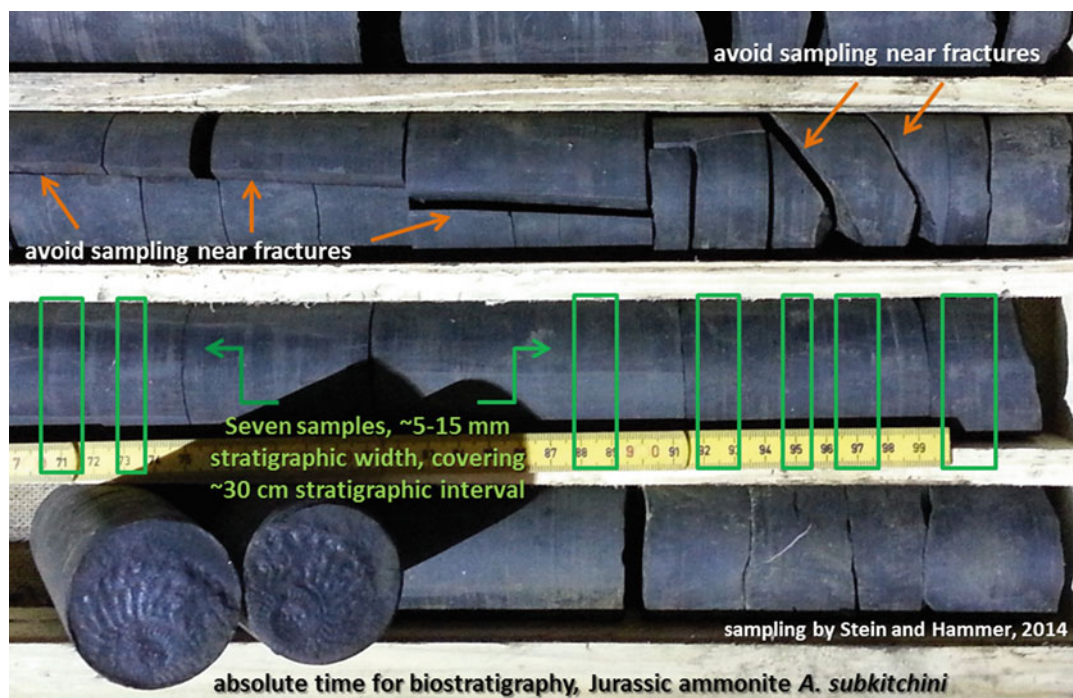


Fig. 6 Sampling shales is the most critical step for Re–Os dating. Drill core showing organic-rich Jurassic *black shale* from Svalbard. The sampling strategy illustrated here is that used by the AIRIE Program. Re–Os analysis of an aliquot from a shale sample acquired from within each *green rectangle* is very likely to yield an accurate and precise isochron age. This particular interval will provide direct age constraints for the Boreal ammonite, *A. subkitchini*

balance is controlled by weathering of carbonates and silicates (Ravizza 2007). The two systems provide complementary data for deducing causes of changes in marine chemistry through time.

Hydrocarbons: What Are We “Dating”?

The proven concentration of Re and Os in organic matter incites immediate interest in the potential for directly “dating” hydrocarbons. Simple thought experiments, however, draw immediate doubts: hydrocarbon systems are by definition open systems. Hydrocarbons are generated by maturation of organic material in a source rock, are expelled, migrate, and may eventually accumulate in a porous reservoir rock with an adequate seal. At what point might Re–Os systematics reveal useful information? How can we know which processes are elucidated by those systematics?

The first attempted Re–Os measurements on organic matter focused on physically separated organic detritus and associated pyrite in the Upper Jurassic Morrison formation (Hannah et al. 2000; Hannah and Stein 2003). All samples yielded high, readily measured concentrations of both Re and Os, with Os and especially Re enriched in organic matter relative to pyrite. Although some useful information could be extracted from closely spaced samples, an approach that subsequently proved useful for dating shales, most of the section was disturbed by open-system behavior. The organic detritus served as a sink for Re and Os dissolved in oxidizing groundwater that flowed through the Morrison sandstones for tens of millions of years.

The first breakthrough was a study by Selby and Creaser (2005b). They analyzed widely spaced samples from the extensive oil sand deposits of Alberta, Canada. A subset of their Re–Os data pointed to an age of 112 ± 5.3 Ma, interpreted as the petroleum emplacement age, and ruling out models suggesting Late Cretaceous hydrocarbon maturation and migration. The conclusions assume that the deposits spanning more than 400 km formed from the same source at the same time, a

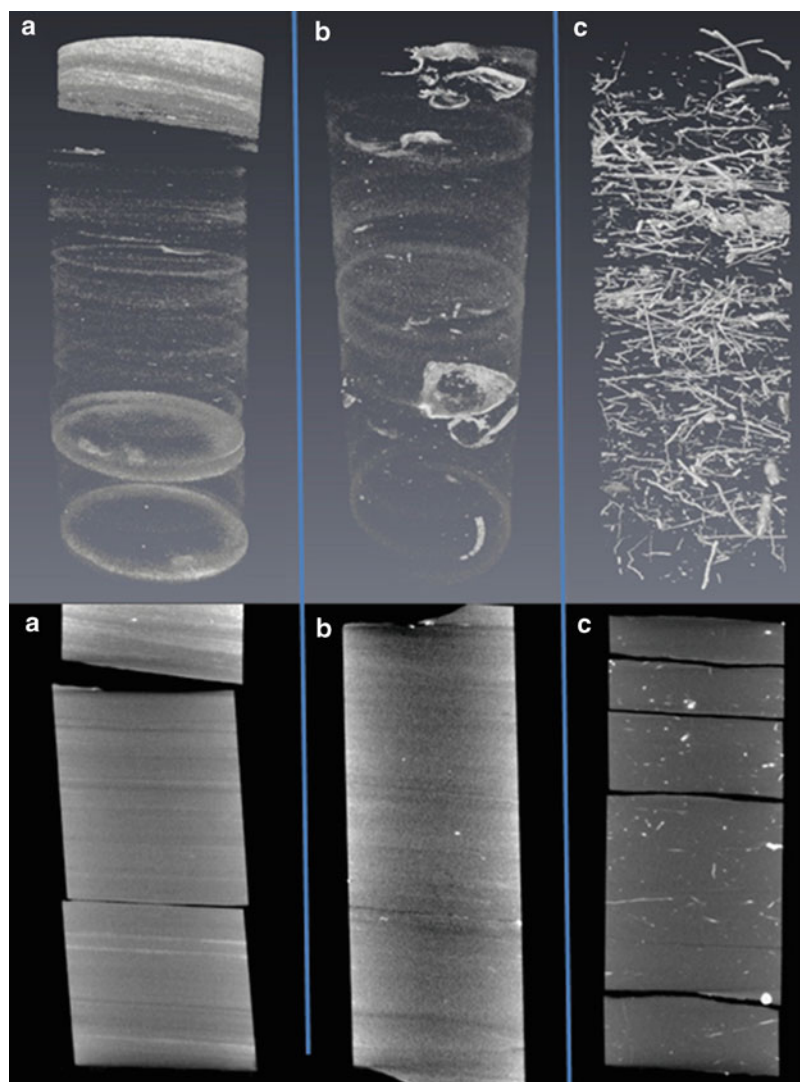


Fig. 7 Sampling shales is the first critical step in Re–Os dating. Three intervals from a drill core, Jurassic black shale, Svalbard. CT images on *top* are paired with corresponding photo of the same drill core piece below. All samples are positioned stratigraphically up toward the top of the page. Cores are 5 cm in diameter. **(a)** IDEAL for Re–Os dating. Beautifully laminated organic-rich black shale with lighter, less organic-rich, siltier intervals visible. **(b)**. SUITABLE for Re–Os dating. Laminated black shale with brachiopod shells concave up indicating settling in quiet water; disseminated bright points are pyritized foraminifera indicating anoxic-euxinic conditions in the water column and bottom waters. **(c)** LESS DESIRABLE for Re–Os dating. Organic-rich black shale shows a myriad of fossil burrows, a record of intense bioturbation. As the organisms work their way into and out of the soft sediment bed, any variation in the osmium isotope composition is stirred at the mm to cm scale. With slow sedimentation rates, this has the potential to introduce scatter into an isochron (Samples collected and imaged by H. Stein and Ø. Hammer)

hypothesis supported by distinctive organic geochemistry. A concern is that 9 outliers of the 26 analyses were excluded on the basis of model initial Os ratios – statistically the same as removing any points not lying close to the isochron derived from all data. In addition, the preferred age was partly controlled by a single analysis (out of five) for one unusual deposit. Nevertheless, their landmark effort constituted a significant advance in analytical techniques and demonstrated that useful age information could be extracted from migrated hydrocarbons.

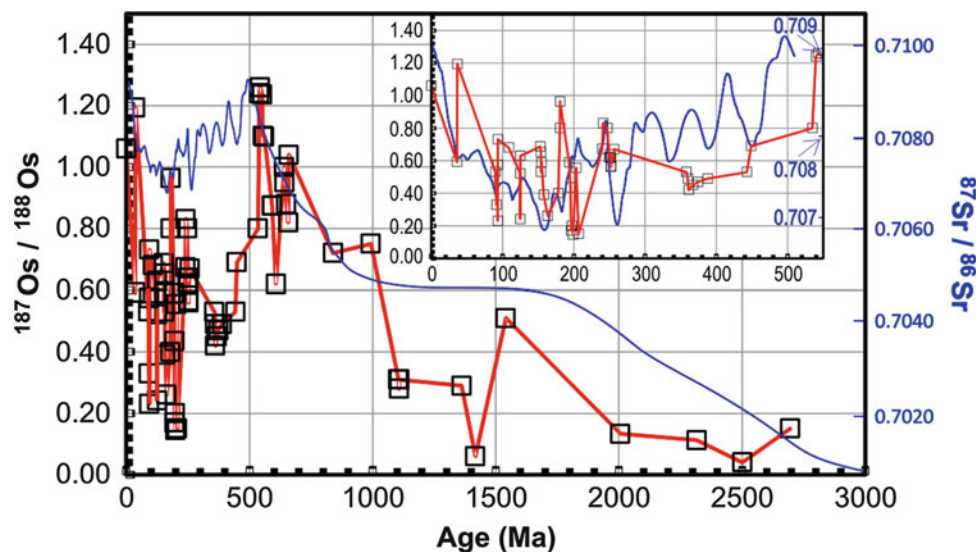


Fig. 8 Variations in the $^{187}\text{Os}/^{188}\text{Os}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in seawater through time. Inset shows the Phanerozoic with an expanded scale. The Os isotope curve shows only initial ratios from isochrons (see discussion in text). The Phanerozoic Sr seawater curve is from Howarth and McArthur (1997) and McArthur et al. (2001); the Precambrian Sr curve is from Shields (2007). The Os curve was compiled by the AIRIE Program from the literature and unpublished data

Subsequent work has documented Re–Os systematics in several hydrocarbon systems, both marine (e.g., Finlay et al. 2011; Lillis and Selby 2013; Hannah et al. 2014) and lacustrine (Cumming et al. 2014). Moreover, geologically reasonable ages for hydrocarbon maturation/expulsion tied to tectonism have been extracted from shales (Stein et al. 2012). Comparison of asphaltene and maltene fractions of individual crude oils (Selby et al. 2007b) and hydrous pyrolysis experiments (artificial hydrocarbon maturation; Rooney et al. 2012) both document minimal differences in both $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ between source rock and extracted oil and among hydrocarbon fractions. Unfortunately, the oil generated by hydrous pyrolysis did not contain measurable Re or Os and was not able to fully replicate natural processes (Rooney et al. 2012). Nevertheless, these studies affirm early work that shows little or no disturbance of Re–Os systematics in organic-rich sedimentary rocks upon hydrocarbon maturation (Creaser et al. 2002 and many subsequent papers on shale geochronology).

A major challenge for deriving age information from oils is generating a spread in $^{187}\text{Re}/^{188}\text{Os}$ from different components of a single oil. Without this, a statistically significant linear regression cannot be achieved, and thus the age and initial $^{187}\text{Os}/^{188}\text{Os}$ cannot be well determined. Selby et al. (2007b) showed that Re and Os are concentrated in the asphaltene fraction, Mahdaoui et al. (2013) further separated asphaltenes by sequential precipitation into strongly and weakly polar fractions. Her results further support observations that separation of lighter oils from asphaltenes does not significantly fractionate Re/Os or $^{187}\text{Os}/^{188}\text{Os}$, but a method is still needed for inducing a spread in Re/Os from a single oil sample. Notably, however, Ni and V concentrations peaked in mid-polarity fractions, while Re and Os dropped continuously from most to least polar. This argues against the commonly held assumption that Re and Os, like Ni and V, are bound in metalloporphyrins.

Re–Os analysis of oils is challenging and very much in its infancy. The potential to place time constraints on maturation, expulsion, and migration of hydrocarbons remains a powerful driver of research.

Summary and Challenges Going Forward

Re–Os geochronology can be used to date earth materials (e.g., sulfides, shales, oils) previously undatable by other isotopic methods. Of pivotal importance, these materials are directly linked to natural resources, both minerals and hydrocarbon, critical to human civilization.

For the immediate future, the challenge is no longer analytical, but geologic. We need to put forward bright and innovative thinking, with the basis for that thinking no longer tied to traditional models, but pointed toward new understanding of how earth's resources are ultimately generated. Re–Os offers more than geochronology. Acquiring an age for an ore deposit, or shale, gives us the last step in a long process. We have the data in hand to start thinking about “how it came about.”

Questions for the future must probe deeper than they have in the past. How can Re–Os be used to link the nascent beginnings of resource formation to the end product that is mined or drained from the earth's crust for profit? This is not esoteric information, but needed information for responsible exploration in the next century. What conditions, far and wide, deep and shallow, make it possible to liberate metals and hydrocarbons? This is part of the slippery question of source – where and how does it start? Our thinking should not be limited to the lithosphere and hydrosphere, but must include atmospheric processes. These three spheres collectively govern resources. Not surprisingly, they also govern the timely issue of climate change.

As a first next step and an easy one to take, reconciling seemingly disparate and non-isochronous data is a good place to start new thinking. There is no such thing as bad data; there is only complexity in data sets that should challenge our imaginations, not prompt us to look only toward the easily interpreted data sets. The barrage of analytical data in the last decade should drive new and thoughtful sampling with different questions in hand.

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Clays and Glauconites (K–Ar/Ar–Ar)

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Introduction

Both conventional K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating methods can be applied to clay minerals. Clay minerals are sheet silicates characterized by their small grain size ($<2\ \mu\text{m}$), thus requiring specialized separation and analytical methods for isotopic dating. Detailed accounts of the conventional K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique have been described by Dalrymple and Lanphere (1969), Faure (1986), Dickin (1995), McDougall and Harrison (1999), and Kelley (2002). The ages of clay minerals can be determined by measuring the amount of the argon isotope ^{40}Ar relative to the potassium content. ^{40}Ar is produced by the radioactive decay of the potassium isotope ^{40}K . Minerals generally contain negligible amounts of argon when they are formed, although small amounts of atmospheric argon may adhere to samples, which can be corrected for by using the known atmospheric $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of 295.5 (Steiger and Jäger 1977). Thus, by measuring the ratio of ^{40}Ar to ^{40}K , and knowing the decay rate of ^{40}K , it is possible to calculate the time since the clay mineral formed.

What Are Clays?

Clay minerals are phyllosilicates; a comprehensive summary of their properties and genesis has been compiled by Srodón and Eberl (1984), Velde (1992), and Meunier (2005). Two clay minerals groups, illite and glauconite, can be dated using isotopic methods. Illite is a general term for a 10 angstrom ($\text{\AA}$) potassium dioctahedral mica-like clay mineral common in sedimentary rocks such as shales and sandstones. Glauconite is an iron potassium phyllosilicate mineral of characteristic green color that occurs in sandstone and carbonate-rich sedimentary rocks (Velde 2004).

As a generalization, illite and glauconite group clays have a dioctahedral mineral structure: $\text{K}(\text{Mg}, \text{Fe}, \text{Al})_2(\text{Si}, \text{Al})_4\text{O}_{10}$, with illite containing $\text{K} < 0.9 (\text{Al})$, and glauconite characterized by the presence of Fe with $\text{K} < 0.9 (\text{Al}, \text{Fe}, \text{Mg})$.

Clay minerals occur in different geological environments as both detrital and authigenic phases. One of the main challenges in clay geochronology is the separation of, and differentiation between, authigenic and detrital mineral phases that is necessary to obtain meaningful geological ages.

Why Date Clays?

Clay minerals are widespread in a variety of geological environments and their occurrence manifests numerous important processes throughout Earth history. Due to their capacity to swell and

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incorporate water, clay minerals are considered important in the evolution of life (i.e., Hashizume 2012). They form significant economic reservoir rocks for water and energy resources (Nadeau 2011). Glauconite is a common authigenic sedimentary mineral and has been used to constrain the geological timescale where biostratigraphic control is limited (Velde 2004).

Clay Dating by K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ Methods: A History and Literature Review

Clauer and Chaudhuri (1995) and Meunier and Velde (2004) summarized the impact, use, and limits of different isotope dating and tracing systems including conventional K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of sedimentary systems. Armstrong (1991) and Clauer et al. (2012) summarized the scientific history and technical developments of the conventional K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ method applied to illite clay minerals. Fundamental nanoparticles of illite with sizes of $<0.02\text{ }\mu\text{m}$ or $<20\text{ nm}$ can be dated successfully (Clauer et al. 1997).

The concept of glauconite K–Ar dating was described by Odin et al. (1982). Smith et al. (1993, 1998) report $^{40}\text{Ar}/^{39}\text{Ar}$ dating of single grain glauconite minerals using micro-encapsulation to address ^{39}Ar recoil. Numerous glauconite dating studies are reported in the literature (e.g., Clauer et al. 2005; Derkowski et al., 2009). However, some controversy exists over the merits of K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ glauconite dating compared to zircons separated from the same stratigraphic units and dated by U–Pb geochronology (Selby 2009).

K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ Dating of Clays: Basic Principles

The K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods allow dating of clay minerals formed since the formation of the solar system (Dalrymple 1991) until a few thousand years before present (Renne et al. 1997), because of the relatively short half-life of about 1,250 Ma ago (Ma) of the ^{40}K isotope. Special care is required in dating young geological samples due to atmospheric $^{40}\text{Ar}/^{39}\text{Ar}$ contamination and error magnification (McDougall and Harrison 1999). Ages are reported to international timescales such as Gradstein et al. (2012).

The age of clay minerals determined by the K–Ar or $^{40}\text{Ar}/^{39}\text{Ar}$ method is valid when the following assumptions are satisfied:

1. The clay mineral must behave as a closed system. The system should not have lost any radiogenic ^{40}Ar produced by decay of ^{40}K , which requires a closed system relative to radiogenic ^{40}Ar and K since clay formation.
2. The radiogenic ^{40}Ar should only be produced by decay of ^{40}K . No ^{40}Ar should have been incorporated into the mineral after its formation.
3. The atmospheric ^{40}Ar should be adjusted to the present-day $^{40}\text{Ar}/^{39}\text{Ar}$ value of 295.5.

Dating authigenic clay mineral crystallization involves a fundamentally different approach from dating detrital clays (Meunier et al. 2004). Theoretical aspects that need to be considered when trying to date authigenic clay minerals include: (1) contamination effects, i.e., mixing with other K-bearing phases, (2) Ar closure, i.e., loss or capture of radiogenic ^{40}Ar during crystallization, (3) the duration of K accumulation, and (4) initial clay mineralogy (illite, illite–smectite).

There is a fundamental difference between the classical mineral cooling model, which is characterized by the Ar “closure temperature”, considered to be of short duration relative to the mineral “life time,” and that pertaining to clays (Faure and Mensing 2005). Dating clay minerals involves the assumption that a newly formed authigenic clay mineral can be dated by isotopic techniques independent of the concept of a closure temperature. This crystallization process can encompass different timescales. If the time interval over which an authigenic mineral has crystallized is shorter than the analytical precision of the method, described in 1 or 2 sigma values, an actual “age” is recorded. However, in some geological case studies, mineral authigenesis and crystallization can extend over extensive time periods, larger than the analytical uncertainties, and an “integrated age” is recorded (Meunier and Velde 2004). Smectite–illite-type minerals growing at any given temperature, labeled as the “Ar retention temperature” (~70 °C), will start the K–Ar radiometric chronometer. Instead of a simple cooling model, the K–Ar dating of clays may be subjected to further recrystallization episodes when the temperature exceeds the crystallization temperature (e.g., Clauer and Chaudhuri 1995, 1998; Meunier et al. 2004).

Ar diffusion effects have been investigated for fine-grained clay minerals. The general theory of Ar diffusion was summarized by Crank (1975) and Watson and Baxter (2007) and its geological applications to the K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods have been outlined by McDougall and Harrison (1999). Huon et al. (1993) described an Ar diffusion model using clay particle morphology as the shape of fine-grained clay minerals will influence diffusion. Models employing cylindrical, planar, and spherical shapes have been applied in investigating or constraining the influence of thermal overprints on the preserved ages in clay minerals. Moreover, only limited Ar diffusion parameters for illite (muscovite) have been published (Wijbrans and McDougall 1986; Harrison et al. 2009).

Clay Dating Methods

K-bearing clay minerals such as illite and glauconite can be dated by the conventional “spiked” K–Ar, the “unspiked” K–Ar, and $^{40}\text{Ar}/^{39}\text{Ar}$ methods.

Classical Spiked K–Ar Clay Dating

For dating K-bearing rocks or minerals, it is necessary to determine the concentrations of ^{40}K and of radiogenic ^{40}Ar on two aliquots of the same sample. Since two splits of any sample are required, a critical assumption of homogeneity of the sampled clays may be violated. Due to the hygroscopic nature of clays, special care has to be taken in the preparation of both K and Ar sample splits. For Ar analysis by noble gas mass spectrometry, sample splits are loaded into clean Al, Cu, or Mo foil, weighed and preheated to 80 °C for several hours to remove moisture, and reweighed using a high-precision balance. The measured dry weight is used in the K–Ar age calculation. For both K and Ar analytical procedures, international mineral standards and blank analyses are performed for quality control purposes. Farley et al. (2013a) developed a new double-spiked K–Ar dating method using a solid ^{39}Ar and ^{41}K spike for K and Ar isotope measurements. This method uses a single mass spectrometer and double spiking requires a single sample aliquot, enabling in situ age determination on other planet surfaces such as Mars (Farley et al. 2013b).

Unspiked K–Ar Clay Dating

The theory and analytical procedures of the unspiked K–Ar method have been summarized by Cassignol and Gillot (1982) and Sudo et al. (1996). The unspiked K–Ar method is able to date geologically very young basalt samples (several kyr) with high atmospheric ^{40}Ar contamination.

With the use of this procedure on clays, the initial $^{40}\text{Ar}/^{36}\text{Ar}$ is calculated from the present atmospheric $^{38}\text{Ar}/^{36}\text{Ar}$ isotope ratio assuming mass-dependent isotopic fractionation during mineral formation.

$^{40}\text{Ar}/^{39}\text{Ar}$ Clay Dating

The basic principles, applications, and analytical methods of dating clay minerals by $^{40}\text{Ar}/^{39}\text{Ar}$ dating are summarized by McDougall and Harrison (1999) and Clauer et al. (2012) and highlight technical challenges related to the micron-scale grain size of clay minerals. Numerous studies have documented the ^{39}Ar recoil phenomenon, resulting from irradiation of the samples by fast neutrons, needed to transmute ^{39}K into ^{39}Ar . This recoil effect, which can cause problems of isotopic loss at the surface of small clay crystals, represents a major disadvantage for clay $^{40}\text{Ar}/^{39}\text{Ar}$ dating, as a precise ^{39}Ar measurement is required to calculate indirectly the amount of K present in the mineral phases. Turner and Cadogan (1974) and Kelley (2002) calculated the distances of ^{39}Ar recoil during irradiation to be a mean of 0.08 μm , refined by Onstott et al. (1995) and Villa (1997). Foland et al. (1992) developed a sample encapsulation method, which allows capture of ^{39}Ar released during irradiation to correct $^{40}\text{Ar}/^{39}\text{Ar}$ ages of illite and glauconite (Onstott et al. 1995; Smith et al. 1993, 1998). Clauer et al. (2012) suggested that the encapsulation method requires a standardization process to allow comparison of data obtained in different laboratories. $^{40}\text{Ar}/^{39}\text{Ar}$ clay dating is controversial as shown by the literature, mainly due to different interpretations of the ^{39}Ar recoil effect (Dong et al. 1995; Yun et al. 2010; Clauer et al. 2011, 2012). In order to minimize ^{39}Ar recoil losses, special sample pre-treatments such as pre-heating under vacuum, compaction under vacuum, neutron irradiation in vacuum, and/or using a different neutron source (e.g., deuterium–deuterium) might offer new analytical pathways in reducing ^{39}Ar recoil effects (Kapusta et al. 1997; Renne et al. 2005).

Applications of Clay Dating

Clay minerals occur in different geological settings and are associated with soil formation, erosion and sedimentation processes, and diagenesis processes that occur during burial from surface locations (Velde 1992; Meunier and Velde 2004). The K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating of diagenetic events in sedimentary systems faces methodological challenges that are discussed within four main applications.

Deep Burial Clay Mineral Authigenesis in Sandstones

Dating of illite offers the prospect of establishing the absolute timing of diagenetic events such as heating or fluid flow events within a sedimentary basin (Pevear 1999).

The radiogenic isotope systematics of sedimentary rocks is complex due to the intimate mixture of minerals of different origins such as detrital phases possibly from a variety of sources and authigenic minerals. It is therefore often difficult to unambiguously interpret measured ages. Special sample preparation techniques involving freeze–thaw disaggregation to avoid over-crushing and extensive size separation to reduce the proportion of detrital phases have been developed (Liewig et al. 1987). Progressive size reduction to submicron size fractions ($<0.1\ \mu\text{m}$ or finer) increases the proportion of authigenic clay phases in the clay component and minimizes contamination. The most reliable isotopic ages for authigenic clay minerals are obtained from the finest size fractions. The validity and importance of the assumptions involved in K–Ar or $^{40}\text{Ar}/^{39}\text{Ar}$ dating of authigenic illite must be carefully addressed, and the sample material characterized using a wide range of methods such as

x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and particle granulometry. Authigenic illite formation is dependent on several parameters including: temperature and pressure ranges and formation fluid chemistry (Hamilton et al. 1992; Wilkinson and Haszeldine 2002). Variables that control the rate of illite growth are temperature, pressure, concentration of reactants (K, Si), rate of supply of reactants, pore fluid velocity, rate of diffusion or active fluid flow, time, and the presence of an aqueous pore fluid. Comprehensive summaries concerning authigenic illite dating can be found in Clauer and Chaudhuri (1995), Clauer et al. (2012), Hamilton et al. (1989, 1992), Worden and Morad (2003), Meunier and Velde (2004), and Meunier et al. (2004).

Smectite to Illite Transition During Burial Diagenesis in Shales

Since Aronson and Hower's (1976) pioneering study focusing on burial diagenesis in the US Gulf coast, numerous studies have investigated other basins (Clauer and Chaudhuri 1995; Girard et al. 1989). The implications for dating of the illite to smectite transition due to burial diagenesis have been summarized in Meunier and Velde (2004) and Frey and Robinson (1999). Illite ages are interpreted as maximum ages because the neoformed illite captured in the finest separated size fraction is formed at the ends of filamentous grains, representing the most recently grown illite, due to Ostwald ripening processes (see Eberl and Środoń 1988; Eberl et al. 1990). Illite grain-size fractions of neoformed illite are mixtures of illite particles formed at different times during growth, and this growth history is usually investigated by dating a range of different grain-size fractions (0.02 to 2–6 µm). Hunziker et al. (1986) and Pevear (1999) discussed the influence of detrital mineral phases on authigenic illite formation in detail for sedimentary systems. To resolve the influence of detrital contamination, a regression method was proposed (Pevear 1999), in which an extrapolated diagenetic age should represent the mean integrated age of the time interval over which illite crystallizes. This method addresses the contamination effect due to intimate authigenic–detrital clay mineral phase mixing at very small grain sizes (<2 µm). In a different approach focusing on the detrital clay mineral end-member, van Laningham and Mark (2011) reported $^{40}\text{Ar}/^{39}\text{Ar}$ standard mineral mixture step heating data and proposed a fine-grained bulk sediment provenance tool that can be applied to date clay minerals.

Glaucconite Dating for Stratigraphic Age Control

Glaucconite formation takes place during deposition of sediment at the water–sediment interface. Glaucconite is therefore an attractive target for isotopic dating of depositional ages of sedimentary rocks (e.g., Odin et al. 1982). Dating of K-bearing clay minerals using the isotopic systems offers the prospect of establishing the absolute timing of sedimentation. To ensure that the dated separates of authigenic glauconite provide meaningful stratigraphic ages, and to avoid any age bias by detrital contribution, Odin (1975) suggested that only glauconites with a K concentration above 5.4 wt% should be used for isotopic dating.

Deformation Events: Brittle Fault and Gouge Zone Dating

Displacement on discrete fault planes often results in the development of fault gouge composed of crushed rock fragments and authigenic illite clay minerals. Numerous studies have highlighted the potential for determining the absolute timing of brittle fault history using isotopic dating techniques including K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating (Vrolijk and van der Pluijm 1999; van der Pluijm et al. 2001; Zwingmann et al. 2004, 2010; Solum et al. 2005; Haines and van der Pluijm 2008; Viola et al. 2013). The understanding of fault processes and specifically the timing and extent of fault gouge formation are important for several reasons: (1) regional correlation of shallow fault activity that is of critical

importance in neotectonic studies, (2) for hydrocarbon exploration as faults may act as either a conduit zone or a seal for fluids and/or hydrocarbons, (3) CO₂ sequestration and possible CO₂ diffusion along fault zones, (4) civil engineering and the evaluation of earthquake hazards, and (5) in assessing the suitability of sites for waste storage such as nuclear waste.

Fault gouge illite grain-size fractions of authigenic origin are mixtures of illite particles formed at different times during growth, and this growth history is also investigated by dating a range of different grain-size fractions. ⁴⁰Ar/³⁹Ar dating of coarse-grained mica is a valuable tool in dating fault processes (Sherlock et al. 2003). However, as outlined, the dating of fine-grained micron size illite mineral fractions is complicated due to ³⁹Ar recoil and the consequent corrections. The inverse relationship between grain size and amount of contamination can therefore make dating of illite fault gouges problematic: the finest grain sizes are normally least contaminated but are influenced by ³⁹Ar recoil and therefore not suitable for ⁴⁰Ar/³⁹Ar dating without encapsulation. Fine-grained illite can easily be dated by traditional K–Ar and can distinguish authigenic and detrital illite clay mineral phases.

Summary and Conclusions

The conventional K–Ar and ⁴⁰Ar/³⁹Ar dating methods have both advantages and limitations:

1. K–Ar dating requires relatively large samples (ca. 50 mg) which can introduce inaccuracy with any sample heterogeneity as two sample aliquots are required for K and Ar analyses.
2. A major obstacle for ⁴⁰Ar/³⁹Ar dating is ³⁹Ar recoil resulting in potential loss of ³⁹Ar, which occurs during irradiation, mostly in the clay mineral size range below <2 μm.
3. ³⁹Ar recoil can be measured using an encapsulation technique that needs to be technically evaluated and standardized.
4. ⁴⁰Ar/³⁹Ar dating and the conventional K–Ar method are valuable tools for clay dating. Both methods have distinct applications in the field of clay geochronology.

Cross-References

- [Ar-Ar and K-Ar Dating](#)
- [Fault Zone \(Thermochronology\)](#)
- [Minerals \(Ar-Ar\)](#)

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Luminescence, Pottery and Bricks

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Definition

The luminescence dating of ceramic materials, including pottery and bricks, is an experimental technique for determining the time elapsed in years since the ceramic material was produced by firing.

Introduction

The luminescence techniques for dating ceramic artifacts have been described in detail by Aitken (1985, 1998). Guidelines produced by English Heritage (Duller 2008) provide a concise overview of applying the method. Although the dating of sedimentary deposits currently forms the main focus of application, the dating of ceramics is discussed in a number of review papers (Liritzis et al. 2013; Preusser et al. 2008; Wintle 2008; Feathers 2003) and also by Wagner (1998).

Historical Perspective

When thermoluminescence (TL) dating was proposed as a new scientific dating method in the 1960s (Aitken 1985; Wintle 2008), the principle, based on the accumulation and storage of trapped charge in crystalline luminescent minerals, was demonstrated using pottery from archaeological contexts. Application to other types of ceramic artifacts, such as curated works of art (Fleming 1979) and ceramic building materials (CBMs), soon followed. The introduction of optically stimulated luminescence (OSL) techniques during the 1980s led to a focusing of research effort on the dating of processes associated with the deposition of (unheated) sediments. This type of application now dominates the field. Although testing of the earliest pottery of Late Pleistocene origin is within the chronological range of the method (Kuzmin et al. 2001), adoption of the method for dating pottery was muted, despite the common occurrence of pottery on many sites from the Neolithic onwards (Orton et al. 1993). For general application, the specialist advice needed for sampling made its deployment less convenient compared with radiocarbon testing, and moreover, the levels of uncertainty in luminescence dates were considered too high to improve on chronologies developed on the basis of pottery typology. Where suitable organic samples are unavailable or where temporal resolution is limited as a result of calibration issues (e.g., the flat spot ca 2500 BP or multiple ranges during the last 500 BP), the dating of many sites has relied on pottery typology, particularly fabric composition. It is in the testing of fabric chronologies where a particular role for luminescence dating of pottery has emerged. Also, after years of dormancy, a role has lately emerged for the dating of brick in standing buildings, and the application to medieval buildings and monuments lacking diagnostic features has become an active area of research.

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Technical Issues

The luminescence age equation (Aitken 1985, 1998), expressed in its most compact form,

$$\text{Age} = \text{Paleodose} / \text{Dose rate},$$

is used to calculate the time elapsed since the chronometer mechanism was last reset (zeroing event), which occurs during the firing process in the case of a ceramic. The age, given in years before the year of testing, is accompanied by an overall uncertainty, given at the 68 % level of confidence (1σ), that is typically between ± 5 and ± 10 % of the age. The paleodose corresponds to the cumulative absorbed dose (in units of gray, Gy) received by grains of luminescent crystalline minerals within the ceramic sample (e.g., quartz or feldspar) since a zeroing or resetting event that is achieved by firing. Since resetting can be achieved for temperatures as low as ca 400 °C (i.e., baked or burnt clay), most well-fired archaeological pottery will have met this condition. Within the relatively short lifetime of a cooking pot, the effect of reheating on a fire has a negligible effect on the luminescence age, but if sherds were redeposited onto a ground surface long after burial and subjected to prolonged heating during a conflagration to temperatures in excess of those indicated above, the date of the destruction event would be obtained. The paleodose is determined experimentally (the basic techniques are discussed in Duller 2008) by applying luminescence techniques to many individual portions of grains of luminescent minerals extracted from the ceramic. The dose rate is usually determined by measuring the concentration of radionuclides present in the sample and the surrounding burial medium, and then applying conversion factors (Aitken 1985, 1998).

Paleodose

Most ceramic materials contain grains of luminescent minerals, such as quartz and feldspar, within the fine (e.g., <20 µm dia.) or coarse (e.g., 100–300 µm dia.) fractions of clays and temper, respectively. Such grains can be extracted in the laboratory by mechanical crushing and, sieving and the application of acid treatments. Typically a minimum of 25 g of ceramic is sufficient for dating measurements, although for some applications this can be reduced significantly by drilling (Fleming 1979). There are important differences in the luminescence properties of the two commonly present mineral types, quartz and feldspar, and this affects their use for dating measurements. In particular, trapped charge, which forms the basis of the chronometer mechanism, is retained without significant loss in quartz over archaeological timescales, whereas for most feldspars, there is a small but continuous loss due to a physical effect referred to as anomalous fading, which causes the age to be underestimated. Although a correction can be applied for the loss, this increases the uncertainty in the luminescence age, and each sample must be tested to establish the extent of fading since the rate of loss varies according to the geological source of the feldspar (Lamothe 2004). Hence, coarse quartz grains are usually preferred when testing ceramic materials, providing they are present in the fabric. Where this is not the case, extraction of the “fine-grain” fraction that usually contains both quartz and feldspar provides an alternative approach. Although feldspars can be selectively removed using acid treatment, the fine-grain technique for paleodose determination tends to be applied routinely without such additional treatment unless part of a methodological study.

Dose Rate

There are two physical volumes of interest when assessing the dose rate to grains in pottery: (a) the ceramic sample; (b) the surrounding medium to a distance of about 50 cm (Aitken 1985). Since the material within the latter contains radionuclides emitting gamma rays contributing ca 25–45 % of the

dose rate, where the proportion depends on the grain size selected for paleodose measurements, an assessment of the radionuclide content of both the ceramic artifact and burial medium is required.

Such assessment is more complex for samples adjacent to layers of soil with differing radionuclide composition or within surface deposits, for example, and for this reason the longstanding advice given (Aitken 1985) to select ceramic samples located within a uniform burial medium remains technically sound (Duller 2008).

For more complex situations, such as shallow or surface contexts, laboratories may use the fine-grain fraction for paleodose determination because a higher proportion (ca 75 %) of the dose rate is due to radioactive sources located within the pottery, and this reduces the dependence of the composition of the burial medium and the extent of overburden on the luminescence age. A further factor that has a bearing on sampling is the moisture content of both ceramic and the burial medium because it has a moderating effect on the dose rate. An average value for the moisture content during the burial period is estimated by the laboratory, and a conservative allowance is usually made for the uncertainty (typically ± 20 %) in the value adopted. Although the maximum moisture uptake of the ceramic, controlled by the porosity, can be measured in the laboratory, it is desirable to obtain samples of both pottery and soil stored with moisture content that is representative of the contemporary conditions within the burial environment. The overall precision in the luminescence age increases (lower uncertainty) in regions where there has been long-term aridity and decreases where the pottery is porous and the moisture content relatively high.

Luminescence Age

There is no internationally agreed specification for the presentation of luminescence dating results, but a listing of technical parameters related to the evaluation of the paleodose and the dose rate normally accompanies the luminescence age in publications and formal reports. The Ancient TL Date List, although no longer actively compiled, provided a systematic compilation of dating results and the last two issues produced included listings of luminescence dates for pottery from Britain (Barnett 1999) and the Southwest of North America (Feathers 2000); more recent guidance concerning aspects of date quotation is included in Duller (2008).

Pottery

Applications of the method to dating pottery can be broadly grouped into those: (a) establishing the date of the deposition of a layer or feature from which the pottery was recovered; (b) testing chronologies developed for pottery typologies; and (c) examining methodological issues, such as the feasibility of dating a previously untested type of pottery. There are several published large-scale dating studies, where the term “large scale” applied here refers to several tens of determinations rather than the several hundreds that could be envisaged with radiocarbon.

The accuracy of luminescence has been tested against independent dating evidence with pottery recovered from sealed contexts where its use before deposition was judged to be short lived. From a statistical analysis of the results for 24 sherds of diagnostic pottery of the British Iron Age (first millennium BC), an average difference of ~ 100 years was obtained between the luminescence dates and the mid-point of the assigned age range in each case (Barnett 2000). Similarly, comparisons of luminescence dates for pottery from short-lived Navajo sites of ca AD 1700 in North America with independent dating evidence provided by dendrochronology produced a favorable outcome (Feathers 2000, 2003).

On many sites, pottery is frequently undiagnostic and found scattered both spatially and temporally within the stratigraphy. Following fragmentation and discard, sherds may be redeposited in the filling of large features such as ditches, pits, and middens. Luminescence dating of pottery from sites in Britain and North America has confirmed that indiscriminate testing of redeposited pottery in large features will produce misleading results where the processes of manufacture and deposition are significantly displaced in time. However, luminescence has a constructive role to play by providing a means of testing chronologies for the onset and persistence of particular fabric types. The luminescence dates obtained in several studies on pottery from sites in Britain (Barnett 2000; Cramp 2006) and North America (Feathers 2009) challenge aspects of previously established fabric chronologies. In one region of Britain (Northampton), the incorporation of fine or coarse shell fragments in temper had been used to distinguish Early and Late Iron Age manufacture, corresponding to a separation of several hundred years, yet the luminescence dates showed that each type of temper was not confined to one of these periods and that the two groups strongly overlapped. In related work, the luminescence dates obtained for sherds of scored ware, although considered to be diagnostic pottery and thought to have been introduced during the 4th century BC, suggest much earlier introduction, in the 9th century BC and therefore a much longer chronological span of manufacture. Comparable issues have been raised by the testing of shell-tempered pottery from North American native sites in the Lower Mississippi Valley (Feathers 2009) and also sand-tempered fabrics from sites in southern Florida (Feathers 2003). While the majority of luminescence dates obtained for shell-tempered pottery from two mound sites were consistent with the assigned date range in the early eleventh century AD on the basis of the cultural assemblage and radiocarbon dates, luminescence dates of up to nearly a millennium earlier were obtained for several sherds from each site. These early dates, although considered enigmatic, flagged the possibility that relict pottery may have been brought to the sites by migrants. AMS radiocarbon dating applied to the carbonate temper to cross-check the reliability of the luminescence dates has since indicated that further work is required to evaluate the extent of a reservoir offset (Peacock and Feathers 2009) correction to the radiocarbon ages. Resolution of this issue represents an important test of both the capability of luminescence to provide a reliable tool for investigating the full temporal ranges of pottery chronologies and to further develop the combined application of independent chronometric techniques when dating pottery (Bonsall et al. 2002). While this aspect is being more actively investigated for North American pottery, work has also progressed sporadically on various sites across Eurasia and East Asia.

Due to the nature of the native North American mound sites, pottery is sampled from contexts that are very shallow or within erosional surfaces, and, as indicated earlier, the fine-grain technique can be applied to reduce the uncertainty in the dose rate, albeit with the attendant issue of anomalous fading to deal with if the feldspar minerals are not removed. The further development of such work has wider methodological implications for sites in other parts of the world where pottery surface scatters form a key component of the surviving archaeological evidence (Dunnell and Feathers 1994; Sampson et al. 1997) and where the testing of organic matter by radiocarbon is highly problematic because of postdepositional disturbance.

While evidence in the literature of research related to the dating of curated artifacts that builds on the early developmental work of the 1970s is sparse, its reactivation in a museum environment is leading to the incorporation of recent advances in experimental and statistical techniques (Zink and Porto 2005).

Ceramic Building Materials

The dating of ceramic building materials (CBM) is a natural extension of the dating of pottery in terms of the experimental techniques applied. Brick has been used extensively in the construction of buildings during the last two millennia. Although the literature is currently limited, examples of dating applications can be found for individual buildings and structures in Europe (e.g., the Czech Republic, Denmark, England, Finland, France, Germany, Italy, and Poland), in Asia (e.g., Cambodia, India, Sri Lanka, Thailand, and Uzbekistan), and in South America (Brazil). While precise dating of high-status buildings of the last millennium can be obtained to within a couple of decades or better, lower-status “vernacular” buildings of the Late Medieval and Early Modern periods in Europe are problematic; dating the construction and phasing of structural changes to better than 50–100 years are often difficult to achieve. In these circumstances, there is the opportunity for luminescence to make a contribution to the dating of brick buildings where an overall uncertainty in the date of ca ± 5 % of the age (± 25 years for a 500-year-old sample) can be approached. When applied to four buildings with reliable documentary and stylistic dating evidence in England, luminescence dating of brick produced extremely encouraging agreement (Bailiff 2007); for six samples taken from these dating control buildings (within the range ca AD 1400–1720), the mean difference between the central values of luminescence and assigned ages was 5 ± 10 years (s.d., $n = 6$).

The value of applying an absolute dating method is illustrated by studies that address wider research questions of chronology that are not bound by regional typologies and also extend beyond application to a single building. For the period following the Roman withdrawal from NW Europe during the early fifth century AD, in particular from Britain and Gaul, there has been a longstanding uncertainty regarding when the manufacture of CBMs was resumed. Recent work with bricks from a group of ecclesiastical buildings in NW France (Blain et al. 2007) and England (Bailiff et al. 2010) indicates that, while in France the practice of brickmaking was maintained during the Early Medieval period, it did not resume until the eleventh century AD in England. The testing of brick from Late Medieval buildings in England has also provided an initially unexpected outcome. Whereas it had been assumed that new bricks were produced for a specific building, the dates obtained for multiple bricks from a single building suggest that recycling was practiced by Late Medieval builders. This is of particular interest to building historians when assessing changes to, and loss of, buildings in urban and rural landscapes. However, the possibility of recycling CBM also provides a note of caution when sampling; in addition to a structural examination of the phasing of a building, the brickwork requires careful inspection for the use of recycled brick. In response to this issue, the possibility of dating the emplacement, rather than manufacture, of bricks has been explored by testing luminescent grains located within either the surface of a brick (Veilleigne 2007) or incorporated in lime mortar (Goedicke 2011) as long as the grains were sufficiently exposed to sunlight before use in construction and subsequently stored in dark conditions until tested in the laboratory.

Summary

After a prolonged period of gestation, two main methodological roles for the application of luminescence dating to archaeological ceramic materials have emerged; the building and testing of pottery fabric chronologies and dating the manufacture of ceramic building materials. When luminescence dates for pottery and brick have been tested against independent dating evidence in well-designed studies, the performance of the method has been found to be reliable and accurate within the estimated experimental uncertainties.

Cross-References

- [Luminescence Dating](#)
- [Luminescence Dating of Archaeological Sediments](#)

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Obsidian Hydration Dating

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Definition

Obsidian: Obsidian is an aluminosilicate, or rhyolitic, glass, formed by rapid cooling of volcanic magma under the proper geologic conditions. As any other glass, it is not a crystal, and thus it lacks the lattice structure typical of crystals at the atomic level. However, glasses do possess some degree of spatial order. Thus, it is an amorphous natural glass that contains pristine water H₂O and sparse crystals of variable sizes of a few microns. The surface is weathered in the atmosphere and the environmental context. Composition: 70–75 % SiO₂, 10–15 % Al₂O₃, 3–5 % Na₂O, 2–5 % K₂O, 1–5 % FeO₃ + FeO (in contrast to iron-bearing glass and silica-enriched leached rinds on obsidian glass recently discovered on Mars that are representative of global processes of explosive volcanism potentially implying widespread acidic leaching on Mars due to oxidizing and acidic solutions). Obsidian rocks were used by early peoples for the making of their tools and implements.

Obsidian Hydration

In its most basic aspect, hydration simply describes the process by which water is absorbed by obsidian and involves physicochemical changes in the glass (Doremus 2002; Anovitz et al. 2008; Liritzis and Stevenson 2012). The six steps of the process involve:

1. Environmental water molecules adsorb on the surface which exhibits roughness at the nanoscale creating a large surface concentration.
2. Absorption into the glass and diffusion into the interstices in the glass matrix occurs. The diffusion process seems to be driven by two properties of the water molecules: a concentration gradient and osmotic pressure or chemical potential. Although it has been suggested that chemical reactions play a role (Doremus 2002, 108 ff.), it is at present a matter of speculation.
3. A water saturation layer is then formed within a short period of time after the start of the diffusion process. Following this period, the saturated layer increases with depth as time progresses. The saturation conditions on the surface represent the average conditions of the physical surroundings for the diffusion system during the elapsed time in a particular archaeological context. It depends on factors that include the kinetics of the diffusion mechanism for the water molecules, the specific chemical structure of obsidian, as well as the external conditions affecting diffusion (temperature, relative humidity, pressure) (Liritzis and Diakostamatiou 2002; Liritzis 2006; Smith and Van Hess 1987).
4. The diffusing molecules stretch the glass matrix, causing an increase in volume in the hydrated region and a stress between unhydrated and hydrated regions.
5. Increased water concentration progresses into the glass, in time, its rate being a function of the initial openness of the glass, temperature, and the dynamics of the process itself.

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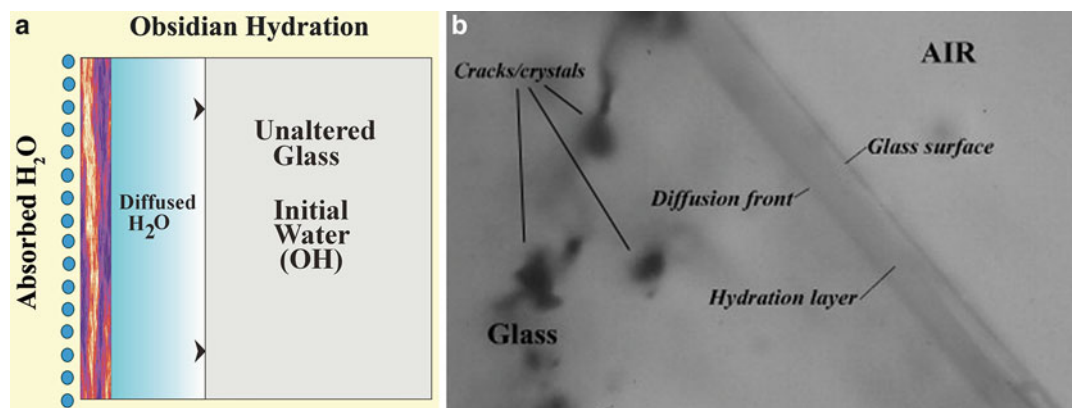


Fig. 1 (a) Schematic diagram of obsidian hydration of diffused water, (b) obsidian hydration rim seen through optical microscopy

6. When the hydrated layer becomes thick enough, typically greater than 20 μm , the accumulated stresses cause the layer to spall off as perlite.

Three general classes of methods have been proposed for measuring obsidian hydration: (a) measurement of water mass uptake or loss versus time by infrared (IR) (Ebert et al. 1991; Stevenson and Novak 2011; Stolper 1982), (b) direct measurement of water profiles versus depth by secondary ion mass spectrometry (SIMS) (Anovitz et al. 1999, 2004, 2008; Liritzis and Diakostamatiou 2002; Riciputi et al. 2002; Liritzis et al. 2004; Stevenson et al. 2004), and (c) observation of the leading edge of the stress zone by optical microscopy (e.g., Friedman and Smith 1960; Friedman and Long 1976; Stevenson et al. 1996).

The environmental water molecules entering obsidian glass depend mainly on (a) environmental temperature, (b) chemical composition, (c) mineralogical structure, and (d) intrinsic water content (see, Silver et al. 1990; Lanford et al. 1979). The deeper the water goes, the greater the time. The higher the environmental temperature in burial sites, the higher the diffusion rate, while for average environmental conditions it is $\sim 1 \text{ mm}/1,000 \text{ years}$ (Figs. 1a, b and 2a, b). Attention is exerted on the precise determination of “hydration front,” i.e., the interface layer between unhydrated and hydrated glass. It is a zone of optical contrast when seen under polarized light, due to the phenomenon of “stress birefringence” (Born and Emil 1980, pp. 703–705). Measurement of this layer can be determined to within $\pm 0.2 \mu\text{m}$ using digital imagery at higher magnification ($800\times$) (Ambrose and Novak 2012). A significant uncertainty can be introduced into the process as a result of poorly defined image quality stemming from improper sample preparation and weakly defined diffusion fronts. It has also been documented that diffused molecular water extends beyond the limits of the optical diffusion front (Stevenson et al. 2001; Tokoyama et al. 2008). Thus, the optical approach does not adequately document the full extent of the diffusion process.

Obsidian Hydration Dating (OHD)

The technique was initiated by Friedman and Smith (1960), where they noted that (a) the exposed surfaces of ancient obsidian artifacts had absorbed water, (b) the hydration birefringent rims were visible under high-power magnification (approximately $\times 500$), and (c) its width was dependent on time, chemical composition (i.e., obsidian quarry), and the temperature. They suggested that

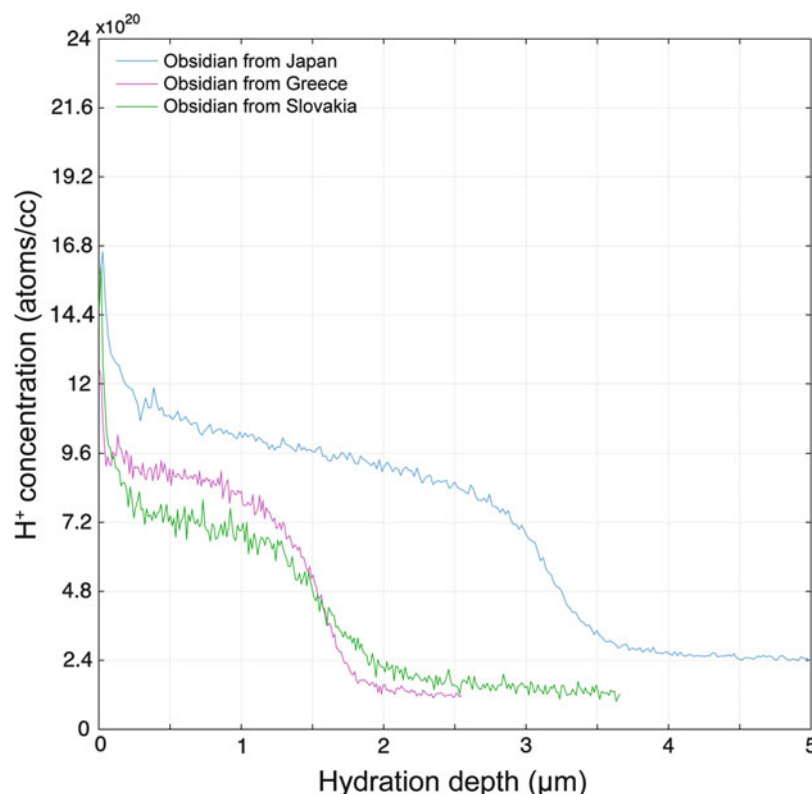


Fig. 2 SIMS H⁺ profiles for three samples from Greece, Japan, and Slovakia

hydration process converts a hydration layer of measured thickness to an absolute date with an established rate for the inward diffusion of molecular water using the empirical Eq. (1):

$$X = (kt)^{1/2} \quad (1)$$

where X is the hydration rim width in microns (μm), k is the hydration rate at a particular temperature/relative humidity, and t is time.

The thickness (X) and the k , which is dependent on the specific archaeological site conditions, are required for age determination.

The hydration rim was initially measured by optical microscopy (Friedman and Smith 1960; Michels, et al. 1983; Stevenson et al. 1989a, b), but inaccuracies in the determination of the end point of the water front (Hull 2001; Stevenson et al. 2002; Anovitz et al. 1999) lead to measurements with other nonoptical techniques, like nuclear reaction analysis, infrared photoacoustic spectroscopy (IR-PAS), and secondary ion mass spectrometry (SIMS) (Stevenson et al. 2000, 2002; Lee et al. 1974; Tsong et al. 1978; Duerden et al. 1982; Liritzis and Diakostamatiou 2002; Anovitz et al. 1999).

The diffusion coefficient was estimated at high temperature (160 °C) and extrapolation to ambient site conditions using the Arrhenius Eq. (3) (Michels et al. 1983; Stevenson et al. 2002; Friedman and Long 1976).

Research subsequent to Friedman and Smith's original presentation has refined the method into two distinct techniques. The simplest referred to as *empirical rate dating* (Meighan et al. 1968; Findlow and Bennett 1978; Meighan 1976; Kimberlin 1976) requires correlating the width to optically measured rims to independent chronometric data, such as ¹⁴C (e.g., Ambrose 1976). The

second more complex and widely applied known as *intrinsic rate dating* requires experimentally determined rate constants and a measure of site temperature (Michels et al. 1983; Friedman and Long 1976; Stevenson and Scheetz 1989; Hull 2001).

The mathematical model utilized in the intrinsic rate OHD was

$$X^2 = A t e^{-E/RT} \quad (2)$$

where X is the depth, A is a source-specific constant, the diffusion coefficient ($\mu\text{m}^2/\text{day}$) is a pre-exponential constant, t is time, and E is the activation energy (calories or Joules per mole), respectively, R is the gas constant (calories per degree per mole, i.e., 1.987), and T is the absolute temperature (Kelvin), in fact the effective hydration temperature (EHT).

Along with this method, the importance of connate water, the compositional indices, and density, in controlling the hydration rate of obsidians, has been demonstrated by several authors (e.g., Ambrose and Stevenson 2004).

Nevertheless, the assumptions made by Eq. (2) are questioned from the sigmoid hydrogen profiles measured by SIMS (Fig. 2).

However, in spite of over 50 years of development and application, of the classical OHD versions has produced consistently reliable results, with the exception of some sites of young age and/or well calibrated to ^{14}C and typology. In some cases, ages have so contradicted other well-established chronometric data that the utility of the obsidian as an independent chronometer had been questioned. The problems with OHD are due to the use of inappropriate analytical techniques, which involved nonsystematic errors arising there from the inherent imprecision of optical measurements, the experimental conditions of estimation of hydration rate, the need for calibration issues, and an improper (empirical) model of the hydration process. The scientific background has illustrated the complexity of the hydration process, and revised working assumptions for OHD have been proposed (Anovitz et al 1999; Friedman and Long 1976; Ambrose 1976; Stevenson et al 2000; Riciputi et al. 2002; Braswell 1992; Hull 2001; Rindings 1996; Liritzis and Laskaris 2012; Liritzis et al. 2004).

An advancement of OHD with a completely new approach – the monitoring of hydrogen profile in obsidian surfaces by SIMS (see below) – suggests that refinement of the OHD technique is possible in a manner which improves both its accuracy and precision and potentially expands the utility by generating chronological as well as palaeoenvironmental and usage data (Liritzis and Laskaris 2011). An earlier attempt of using nuclear reaction to monitor H^+ by depth has not been followed up (Tsong et al. 1981).

Another recent example of progress with classical OHD is based on accurate measurement by IR-PAS and calculation of diffusion rates. The rate of environmental molecular water diffusion depends on the total structural water content of the obsidian found in the bulk glass. As the process of mass uptake is a function of temperature, pressure, and openness of the glass matrix as measured by intrinsic water concentration, mass gain or loss proceeds proportional to t^n , where t is time and n is an exponent lying between approximately 0.5 and 0.6 shown by IR-PAS analysis in a series of 90 °C isothermal laboratory hydration experiments (Stevenson and Novak 2011). Later on, Stevenson et al. (2013) have applied this developed calibration to estimate hydration rates for obsidian based upon the structural water content of the glass as determined by IR-PAS to 53 Rapa Nui, Easter Island, Chile. Here, the Arrhenius constants (i.e., pre-exponential, activation energy) may be estimated from $\text{H}_2\text{O}t$ (see below).

Accuracy of Hydration Rim Measurements

In a satisfactory laboratory technique, accuracy is not limited by resolution of the microscope to $\sim 0.25\ \mu\text{m}$, but probably lies in the range of $0.05\text{--}0.1\ \mu\text{m}$, which is consistent with data reported. In a practical sense, measurement accuracy is more likely limited by the material properties of the obsidian. In any case, the accuracy of rim measurement is not a large contributor to the error in computed age in OHD (Rogers 2010), who points that computing a hydration rate is *not* a regression problem, however, but a problem of parameter optimization.

However, the apparent rim accuracy thus achieved is not the main factor in age determination. Each data point is a combination of valid data and experimental error, with major errors arising from site formation processes, association with radiocarbon or luminescence dating or the archaeological typology and obsidian, uncertainties in temperature, and fluctuations in the hydration rate which are not accounted for.

OHD Based on SIMS and IR-PAS Methodological Approaches

Initiated by Tsong et al. (1980; 1981), OHD based on SIMS has been followed by dozens of articles on the application of SIMS on obsidian artifacts but most on the determination of hydration layer, the diffusion of cations, and the dating. The direct measurement of the water profile measurement is generally performed by SIMS or the IR-PAS. The principle is to measure the concentration of H^+ ions, as a proxy for water, as a function of depth. The depth of penetration is typically measured by the end point (tail) where the water concentration has fallen to the pristine water concentration value at the surface.

Two teams at Oak Ridge (USA) and Rhodes (Greece) relied on the modeling of the H_2O concentration profile as a function of hydration depth, but following them in different ways. As a result, the ODDSIMS and the SIMS-SS coined versions were produced, respectively (Anovitz et al. 1999, 2004; Liritzis and Diakostamatiou 2002; Liritzis et al 2004; Liritzis and Laskaris 2009, 2011).

In using SIMS, an ion beam (usually Cs) bombards the obsidian surface. (The dating is based on the concentration of H as a proxy for H_2O versus depth) (Fig. 3).

The use of SIMS on obsidian surface investigations, although relatively infrequent, has produced great progress in OHD dating. In essence, it is a technique with a large resolution on a plethora of chemical elements and molecular structures in an essentially nondestructive manner (Liritzis and Laskaris 2011).

Anovitz et al. (1999) presented a model which relied solely on compositionally dependent diffusion, following numerical solutions (finite difference (FD) or finite element) elaborating on the H^+ profile acquired by SIMS. A test of the model followed using results from Mount 65, Chalco in Mexico, by Riciputi et al. (2002). This technique used numerical calculation to model the formation of the entire diffusion profile as a function of time and fitted the derived curve to the hydrogen profile. The FD equations are based on a number of assumptions about the behavior of water as it diffused into the glass and characteristic points of the SIMS H^+ diffusion profile. In fact, the depth of the half-amplitude point of S-like H^+ profile is found to be proportional to t^n , where t is time and n is an exponent lying between approximately 0.6 and 0.7 (Anovitz et al. 1999, 2004; Stevenson and Novak 2011). The half-amplitude measurement is again a function of temperature and openness of the matrix; however, since the measurement is made to a half-amplitude point, i.e., a relative measurement, the technique is not sensitive to the total amount of water present and should not be affected by pressure.

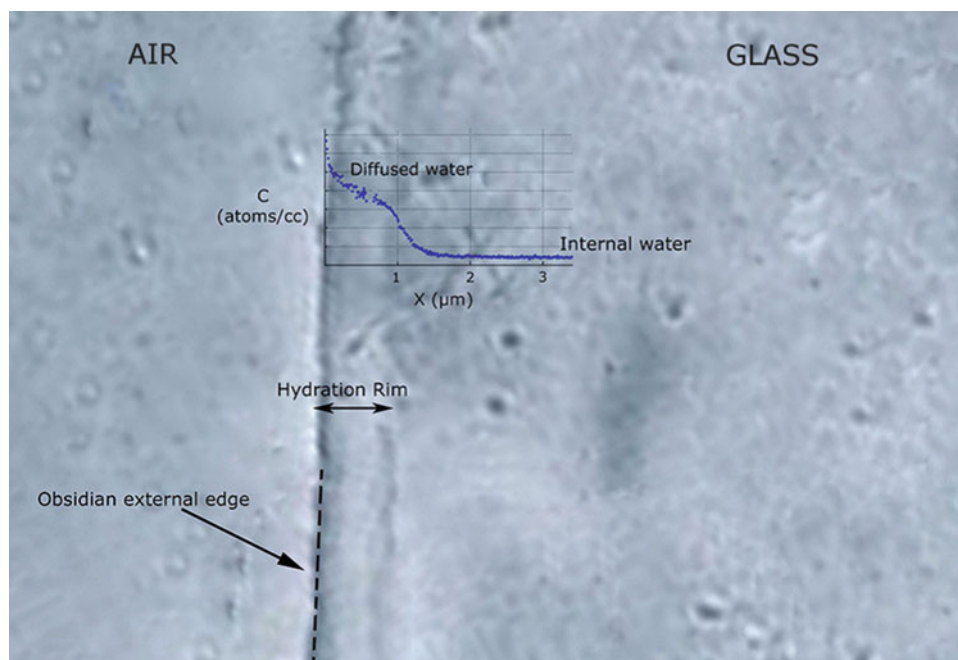


Fig. 3 Overlapping of SIMS H^+ profile in atoms/cc versus depth, on the hydration layer (rim), into the obsidian glass (Liritzis and Laskaris 2011)

In Rhodes, Greece, one dating approach is based on modeling the hydrogen profile, following Fick's diffusion law, and an understanding of the surface saturation layer (surface saturation, SS) and surface topography (Liritzis 2006; Liritzis et al. 2004; Liritzis and Laskaris 2009). The saturation conditions on the surface represent the average conditions of the physical surroundings for the diffusion system during the elapsed time in a particular archaeological context.

It has been shown (Liritzis 2006) that all of the H^+ profiles are broadly similar in form; however, this is their only shared property. Despite the fact that they are derived from the same type of geological material, close inspection of the shape of the profiles suggests that definite differences are present. These which are derived from the significant environmental impact as well as intrinsic effects may alter the form of the SIMS hydrogen profile. It is these slight variations in the profile that are case specific, and this is the important observation that the calculated age by SIMS-SS method relies upon. Therefore, each age calculation is based on this diffusion profile, which is unique for every obsidian sample. There are three advantages to this fully intrinsic procedure: (1) the final shape of the hydrogen profile, properly modeled, incorporates two of the principal external and highly variable environmental parameters, those of temperature and humidity; (2) the use of SIMS instrumentation to measure surface hydration layers results in high precision thickness (depth) values with an error of 0.02–0.05 μm depending upon the degree of surface roughness; and (3) absolute age estimates may be calculated. The currently used two methods, one based on SIMS (namely, SIMS-SS, SS for surface saturation) and the other on IR-PAS, are briefly described below.

The SIMS-SS Method

The water diffusion coefficient at any particular moment is expressed by the first derivative of the hydrogen profile. Its inverse ratio is the apparent hydration rate. The average depth of surface saturation layer X_s and corresponding saturation concentration C_s obtained from the determination of the SS layer gives the overall error attached to the SIMS-SS ages.

Using the end product of diffusion, a phenomenological model has been developed, based on certain initial and boundary conditions and appropriate physicochemical mechanisms that express the H₂O concentration versus depth profile as a diffusion/time equation. The modeling of this diffusion process is a one-dimensional phenomenon, where the H₂O molecules invade a semi-infinite medium in a perpendicular direction to the surface. The model is based on the idea that in the SS layer located near the sample surface, that is, in the first half of the sigmoid curve, the C is assumed as constant along a very short distance. Thereafter, C gradually decreases following the trend of the sigmoid. In brief, the three principles used for dating are (a) the comparison of a nondimensional plot with a family of curves of known exponential diffusion coefficients; (b) the correlation between the rate of transfer (diffusion) from the surface with the diffusion duration, the saturation concentration C_s, the intrinsic (pristine) water concentration C_i, the diffusion coefficient D_s (defined the flux/gradient, where gradient or tangent = dC/dx), and the following Boltzmann's transformation and auxiliary variables; and (c) the modeled curve of diffusion profile (concentration versus depth) of Eq. (3) (see Liritzis et al. 2004; Liritzis and Laskaris 2012).

$$C = e^{a+bx+cx^2+dx^3} \quad (3)$$

The dating in Eq. (4) that has been proposed incorporates all the abovementioned parameters:

$$T = \frac{(C_i - C_s)^2 \left[\frac{1.128}{1 - \frac{0.177 k C_i}{C_s}} \right]^2}{4 D_{s, \text{eff}} \left(\frac{dC}{dx} \Big|_{x=0} \right)^2} \quad (4)$$

where C_i is the intrinsic concentration of water, C_s the saturation concentration, D_s = dC/dx the diffusion coefficient for depth equal to zero, D_{s,eff} the effective diffusion coefficient empirically derived from a set of well-known ages and Eq. (5) as the effective value of the diffusion coefficient D_s for C = C_s, and k is derived from the family of Crank's curve. It is:

$$D_{s, \text{eff}} = a * D_s + b / (10^{22} * D_s) \quad (5)$$

where D_s = (1/(dC/dx)) * 10⁻¹¹ assuming a constant flux and taken as unity (Liritzis and Laskaris 2009; Liritzis 2006; Brodkey and Liritzis 2004). Equation (5) and assumption of unity are a matter of further investigation.

Often, the obsidian surface at the micro- and nanoscale is not smooth, and this influences the diffusion of water and, as a result, the SIMS profile. Polarized light microscopy (PLM) and atomic force microscopy (AFM) (Fig. 4) have been used to examine the obsidian surface and investigate any correlation between the surface roughness and the SIMS measurements (Liritzis et al. 2007). As proposed by Liritzis et al. (2008a, b), a linear regression fit in the diffused region defines the dispersion which reflects the degree of surface roughness. The smoother the surface, the less pronounced the dispersion of the data points to either side of the trend line and the smoother the SIMS diffusion profile. The surface roughness measured by the AFM instrument is linearly correlated with the standard deviation of the residuals between the data points (H⁺ values of g/mol or atoms/cc) and the linear fit in the diffused region of SIMS. This proportionality aids the selection of appropriate obsidian samples/surfaces for dating and also for the proper choice of the spot where the SIMS analysis is performed. Last, the smooth variation of other monitored cation

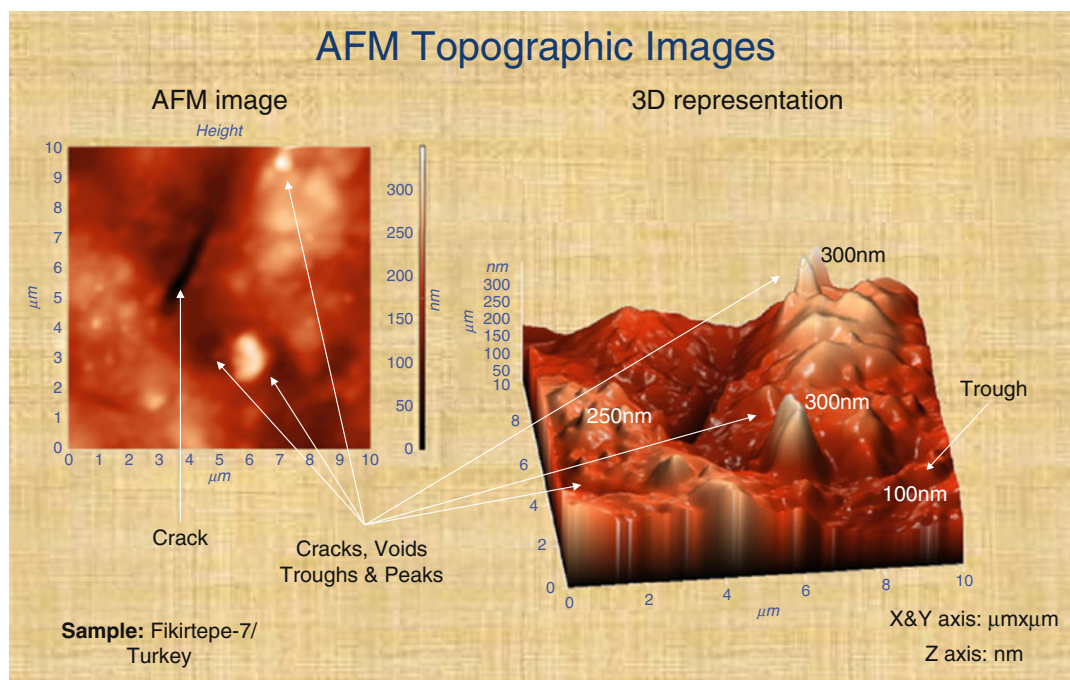


Fig. 4 Atomic force microscopy on obsidian surface indicates surface roughness, most significant parameter for accurate SIMS H⁺ profiling (Liritzis and Laskaris 2009)

profiles (K, Fe, Si, Mg, F, Al) and mapping of ion rastered surface areas act as criteria for acceptable and safe further numerical evaluation of H⁺ profiles.

The validity of these new procedures is tested through a comparison with independently derived age determination. A suite of samples from Easter Island (Chile), Mexico, Greece, Japan, Asia Minor, and Hungary, ranging from few hundreds to 30,000 years ago, have been used, derived from archaeological contexts dated by the radiocarbon method or ceramic associations. Indeed, the convergence between the two dating methods is high (Figs. 5). The SIMS-SS age estimates fall within the expected age ranges for the archaeological contexts for all samples (Liritzis and Laskaris 2009; Liritzis 2010). Table 1 gives an example of two dates by SIMS-SS.

Obsidian Hydration Dating by IR-PAS

The application of IR-PAS (infrared photoacoustic spectroscopy) to the dating of obsidian was proposed as a solution for two central methodological problems associated with OHD using optical microscopy. *First*, optical measurements of hydration layer thickness from prepared thin sections rely upon a visual assessment of hydration layer strain birefringence to establish a depth of penetration. This strain is a secondary effect created by a volume expansion associated with molecular water diffusion that slows the passage of light through the hydrated layer. *Second*, it has been documented in numerous instances that the rate of water diffusion is significantly impacted by the amount of total structural water found within the glass matrix (Karsten and Delaney 1981; Zhang and Behrens 2000; Tomozawa 1985). Calibrations have been developed that correlate the concentration of structural water with laboratory hydration rates at lower temperatures (90 °C) (Stevenson et al. 1998; Stevenson and Novak 2011).

With the IR-PAS method, an absorbance spectrum associated with the vibrational modes of glass functional groups (Si-OH, Al-OH) and water peaks (OH, H₂O) is produced; at 3,570 cm⁻¹, it represents a combination band for OH/H₂O, and the band at 1,630 cm⁻¹ reflects the molecular

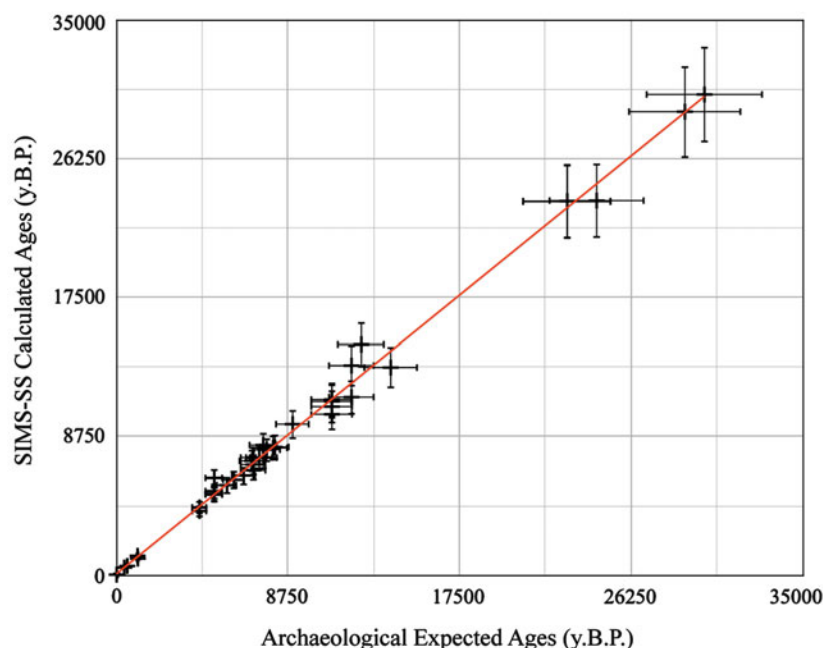


Fig. 5 SIMS-SS versus ^{14}C /archaeological ages for obsidians all over the world (Liritzis and Laskaris 2011)

Table 1 The SIMS-SS dates for two samples from Ikaria Island, Greece (Kerame site), without any other chronological control (From Liritzis and Laskaris 2012)

No.	Lab. No./site	Sampling details	X_s (cm)	C_s (grmol/cc)	C_i (grmol/cc)	e^k	$D_{s,eff}$ (cm^2/year)	Age SIMS-SS (years BP)
1	RHO-891 Kerame, Ikaria	T,C, Spit 4 Sq. 5 + 6	$3.1486\text{e-}5 \pm 1.87\text{e-}6$	$0.00129197 \pm 1.79\text{e-}5$	$0.000106014 \pm 6.24\text{e-}6$	360	$1.1365\text{e-}12$	$11,085 \pm 3,282$
2	RHO-892 Kerame, Ikaria	Trench D Spit 4	$4.90433\text{e-}5 \pm 2.24\text{e-}5$	$0.0007287 \pm 2.24\text{e-}5$	$9.8763\text{e-}5 \pm 4.44018\text{e-}6$	80	$3.42\text{e-}13$	$10,152 \pm 1,643$

concentration of H_2O whether structural molecular or diffused molecular water (Newman et al. 1986), as well as the structural water content of unhydrated region. The method is partially destructive since the artifact or flake must be cut to fit within the sample chamber and the IR-PAS peaks can be impacted by micro-cracks or voids within the glass that trap and retain molecular water. Stevenson et al. (2001) developed a calibration between IR-PAS intensity at $1,630\text{ cm}^{-1}$ and percent molecular water content ($\%\text{H}_2\text{Om}$), using polished and parallel-sided obsidian samples with a range in total water content from 0.09 % to 1.57 %. The rate constants are then calculated for an archaeological specimen. The 90°C diffusion coefficient (D) and activation energy value (E) are estimated from the obsidian total structural water content ($\%\text{H}_2\text{Ot}$) in weight percent concentration. The quantity k in age equation is estimated from the Arrhenius equation:

$$k = D \exp(-E/RT) \quad (6)$$

where D is the diffusion coefficient for H_2Om at 90°C , E is the activation energy in J/mol , R is the gas constant (8.314 J/mol K), and T is the hydration temperature (Kelvin). The archaeological site

temperature is determined for this application by direct measurement of soil temperature using cells monitoring T for 1 year. The resulting rate was then used to estimate ages for obsidian artifacts.

Recently, 52 obsidian specimens were measured at two sites of Rapa Nui Easter Island, Chile. Average measurements per parameter and deduced age for the sample 23 of site 15–233, test unit 2 were as follows: temperature as a function of specimen depth (not really an effective hydration temperature), 22.1–23.4 °C; PAS hydrated 1,630 cm⁻¹, 0.1025; %H₂Ome (environmental diffused molecular water) in hydration layer, 0.10 %; 3,570 cm⁻¹ PAS polished, 0.1313; structural %H₂Ot, 0.89; D at 90 °C as %H₂Ome^{0.5}/day, 0.000000118 (exponent 0.5 as in Eq.(1); E (J/mol), 84.450; diffusion rate estimated (%H₂Ome^{0.5}/year), 0.000027000; and dates, A.D. 1,419 ± 30 to A.D. 1,842 ± 30 years. Ages resulted in an acceptable degree of agreement with radiocarbon ages that those parameters can be used for other obsidian specimens excavated at the island (Stevenson et al. 2013).

However, at Rapa Nui, three problems come into play, which may be applicable to all methods. (i) Handling difficulties and the lack of artifact clarity call for different sampling methods to obtain structural H₂Ot and diffused H₂Ome concentration values.

The amount of damage to an artifact may be substantial when the thick section is removed, and in the worst of cases, small obsidian flakes may be completely destroyed or too small to be processed at all. In addition, opaque obsidians, which constitute a large proportion of the world's natural glasses, may not achieve clarity even after thinning glass thick sections to 0.5 mm. These same issues apply to processing a second subsample in order to measure the hydrated surface. (ii) Laboratory applications of obsidian hydration dating include multiple sources of error that impact the precision of a final age determination. The precision errors cannot simply be added to estimate a total error because the variables are independent of each other with the first associated with a concentration value and the second to a rate coefficient. The latter however seems to coincidentally provide a correct value from hydration experiments at 90 °C, while the used annual results of ambient T need further clarification. (iii) The EHT is a problem that in the above example at Easter Island seems to be overcome due to the short time archaeological intervals involved, since present T measurements are similar for the last say 2–5 hundred of years, but cannot be as such for a few thousand of years BP.

Diffusion Mechanisms in Obsidian

Considerable complexity of phase states has been indicated by a wide range of variability of properties from obsidian sources. The exact mechanism by which water diffusion in such amorphous glasses takes place, by either mechanical transport or molecular interconversion, is still subject to research (Doremus 1969, 2000, 2002; Nowak and Behrens 1997; Zhang et al. 1991; Zhang and Behrens 2000; Crank 1975). In either case, diffusion reaction is described approximately by Eq (7):

$$\partial W / \partial t = \partial (De \partial W / \partial x) / \partial x, \quad (7)$$

where W is concentration of total water, H₂O + OH⁻ (Doremus 2002, pp. 109–110; Zhang and Behrens 2000), and De is the effective diffusion coefficient given by Eq. (8):

$$De = 2WD / \beta, \quad (8)$$

where D is a constant diffusion coefficient characteristic of molecular H_2O and β is a proportionality constant related to the Ostwald solubility of water in obsidian (Doremus 2002, pp. 78, 110). The general solution of Eq. (7) requires numerical techniques and has been a subject of various considerations (Crank 1975), while an elaboration based on Fick's law has led to new age approaches by SIMS (Liritzis et al. 2004; Liritzis and Laskaris 2011; Anovitz et al. 1999).

Accelerated hydration experiments have shown that the diffusion of water is a complex and dynamic process (Anovitz et al. 2004; Stevenson and Novak 2011). The very early stages of hydration exhibit a high surface water concentration, a declining diffusion coefficient, and an advancing diffusion front. This change may be due to glass surface relaxation as the stress that built up in the near surface region is released. However, there may be a difference in the mechanism behind the early stage of water diffusion that differs from the longer-term developmental process.

Following the work of Doremus (2000, 2002) and Liritzis (2006), Stevenson and Novak (2011) hypothesized that H_2O_t creates a more open glass structure which allows water molecules to pass through "gateways" in the silica tetrahedra. It was their observation that the greater the concentration of H_2O_t , the faster the diffusion rate of ambient water (H_2O_m) into the obsidian surface.

Water enters obsidian glass at environmental temperatures as molecular H_2O and as hydroxyl OH formed by reaction with the glass silicate structure. It is believed that the occurrence of greater amounts of Si-OH in the network (silanols, referred to the intrinsic water molecules which may be present as OH- with the siliceous network) may weaken the neighboring Si-O-Si bonds, causing them to easily break, and therefore lower the overall activation energy (Brückner 1970; Ericson et al. 2004). However, the latter view may be revised as silanols seem to follow hydrogen sigmoid profile due to diffused water (see, Fig. 9, Liritzis and Laskaris 2011).

At any rate, as water enters the glass network, the structure is depolymerized and hydrogenated and silanol ions are formed (Si-OH) and allow additional water to enter the glass at a faster rate, while in the course of time, chemical reaction follows Fick's law. This changing diffusion coefficient results in the formation of the characteristic S-shaped concentration-depth profile (Fig. 2).

According to another model, H_2O molecules choose various diffusion paths in a nonhomogeneous way, as the size-dependent mechanism assumes that water molecules of radius $R_w = 0.15$ nm occupy interstitial sites of the obsidian and pass through "doorways" of radius R_D jumping from one doorway to another. The $R_D = 0.1$ nm derives from the equation regarding activation energy E , which is recognized as the elastic energy necessary to dilate a spherical cavity from radius R_D to R (Doremus 2002; Liritzis 2006). The rate at which this process occurs depends upon the intermolecular distance of the host material matrix compared to the size of the diffusing species.

This diffusion process forms an external layer as water leaves the atmosphere and humid sediment and diffuses into the glass structure. In particular, the surface saturated layer (SS layer) is formed in the first 1–3 μm of the obsidian surface through two diffusion mechanisms. The first mechanism transfers the ambient water from the environment into the exterior surface of obsidian, and the second mechanism is responsible for the diffusion process into the interior of the artifact (Liritzis and Diakostamatiou 2002). The mechanism of water diffusion in obsidian and the exponent of time in Eq. (1) are still a matter of investigation.

Discussion of Some Issues Related to Conventional OHD

A variety of strategies have been developed over the years to calibrate the movement of ambient water into a glass, to take into account the composition of the glass, and to model the environmental

history of the artifact context (e.g., temperature, humidity). In essence, the rate of hydration is dependent on the obsidian chemistry, the intrinsic water content of the glass, the temperature and relative humidity, and the chemistry of the diffusing water (Friedman and Long 1976; Ambrose 1984; Mazer et al. 1991; Friedman et al. 1994; Stevenson et al. 1998; Stevenson et al. 2002; Ambrose and Stevenson 2004; Rogers 2008, 2012).

Presently, the exponent of Eq. (1) is being questioned as non-applicable to all environments, and the determination of the diffusion coefficient from extrapolation of laboratory hydrated obsidians down to ambient conditions from the Arrhenius plot is considered as insecure (Anovitz et al. 1999; Stevenson and Novak 2011; Liritzis and Laskaris 2011). Several decades of research illustrated the complexity of the hydration process, and *revised* working assumptions or disillusiones for OHD were proposed (Mazer et al. 1991; Stevenson et al. 1998, 2000; Rogers 2007; Ridings 1996). In spite of many years of development and application, mainly from research groups in the USA and Australia, it appears that neither approach has produced consistently reliable results. In some cases, ages have so contradicted other well-established chronometric and/or typological data that the utility of the obsidian as a chronometer has been questioned (Anovitz et al. 1999; Ridings 1996; Liritzis 2006; Rogers 2008; Eerkens et al. 2008).

Although OHD seemed to give good relative ages in some case studies as in Easter Islands (Stevenson et al. 2000; Stevenson et al. 2013), practitioners of the measurement pointed to significant errors in other cases (Ridings 1996). The problem of determining accurately the hydration thickness is solved with new techniques such as infrared spectroscopy (IR), SIMS. Infrared spectroscopy has been used to measure the bulk water content of obsidian (Newman et al. 1986; Zhang et al. 1996) with the photoacoustic method (IR-PAS) used to quantify the depth of surface water diffusion (Stevenson et al. 2001, 2002; Stevenson and Novak 2011). The latter approach to hydration layer depth assessment has been calibrated relatively to SIMS and shown to have a higher precision and accuracy than obtainable by optical microscopy (Ambrose and Novak 2012).

In certain cases, extensive lab experiments using the same obsidian source, diffusion rate, and average environmental hydration temperature (effective hydration temperature) using temperature cells yielded satisfactory ages. These were controlled by available ^{14}C ages and ceramic typology, e.g., for south coast of Peru, using petrographic microscopic rim measurements (Eerkens et al. 2008), and Hopewell culture (Stevenson et al. 1998, 2004), using rim measurements by SIMS.

To summarize, the early problems with OHD were partly due to inappropriate analytical techniques involving (i) nonsystematic errors arising from the inherent imprecision for optical measurements, (ii) the experimental conditions and data of estimation of hydration rate, and (iii) on a theoretical plan an improper model of the hydration process.

Laboratory-induced hydration does not produce commensurable results with the in situ-induced hydration and/or silica dilution (Morganstein et al. 1999; Bartholomew et al. 1980). This was the case even when using a long-term artificial aging experiment with the obsidian samples from three separate volcanic provinces in Papua New Guinea exposed in normal air and water vapor pressure to controlled temperatures of 10 °C, 20 °C, 30 °C, and 40 °C, for up to 26 years (Ambrose and Novak 2012). Nevertheless, the latter confirm the value of the strategy by providing basic hydration rate constants for obsidian specimens from each of the three major Papua New Guinea sources. But in an archaeological context, these data still require calibration for an optical microscopy hydration measurement. SIMS provides an enhanced measurement system and is combined here with experimentally determined rate constants to independently cross-check radiocarbon dates and site temperature calculation at a ~2,100 BP archaeological site from Papua New Guinea. In fact, Ambrose and Novak (2012) noted that the error figure in age indicates the wide divergence from hydration reading error alone, while additional temperature-based error is even greater than the reading error

by a few hundreds of years and underlines the critical influence of temperature in attempting to derive absolute age values from obsidian hydration dating.

At any rate, the involved age in Eq. (1) is still empirical, surely far apart of the more satisfactory phenomenological approach and certainly not well substantiated by a scientific approach (Brodkey and Liritzis 2004).

Sources of uncertainty in OHD include hydrous and compositional chemistry, humidity, rim measurement, temperature history, diffusion rate variability due to intrinsic water and determination by extrapolation from higher temperature experiments, site formation processes, and age errors from comparative methods (with ^{14}C , archaeological typology) which affect the validity of the age-rim association.

Nevertheless, in spite of rigorous statistical modeling and error propagation, the evaluations of all sources of error impart uncertainties in each variant factor such that the span of uncertainties may sway between extreme percentages of the order of some 10s of a percent. The issue of considering any individual specimen and burial location as a unique case is a rule. Along this direction, calibration models per excavated site are always useful but are cumbersome and timing. A brief evaluation of main factors related and affecting the traditional OHD is described below.

Temperature

Perhaps the biggest problem is temperature, since the hydration process is strongly temperature dependent and the temperature history of an artifact can never be completely known. Past historical temperatures vary over time, both annually and diurnally, and hydration rate of obsidian is temperature dependent. The effect of the varying temperature is coined by the concept of *effective hydration temperature* (EHT), defined as the constant temperature which yields same hydration results as the actual time-varying temperature over the same period of time and can be computed from the time average of D (Rogers 2007). Because of the mathematical form of the dependence of hydration rate on temperature, $\text{EHT} \geq T$ mean. In fact, few degrees in error of EHT in the Arrhenius equation (embedded in Eq. (2)) produce errors of several centuries. For an activation energy (E) of 85 KJ/mol, the error in age for $\pm 1^\circ\text{C}$ is ± 11 – 13% , for $\pm 2^\circ\text{C}$ is $\pm 25\%$, and for $\pm 3^\circ\text{C}$ is around $\pm 37\%$. The well-known modifiers of obsidian hydration rate with temperature (the others being chemical composition and water vapor pressure) may be accounted for, but none is sufficient for precise prediction of hydration rates. For this reason, obsidians still need to be independently assessed for their own specific rate determination. On the other hand, another reported temperature approach using a set of calculated temperature parameters for one site based on a regional temperature scaling analysis contains uncertainties too and can further be corrected for first-order changes in paleotemperature if proxy data are available (Rogers 2010, 2012; Rogers and Yohe 2011; West et al. 2007). Even so, it is unlikely that EHT can be corrected much better than $\pm 1.0^\circ\text{C}$ (Rogers 2007). EHT includes the effects of temperature history in one parameter; furthermore, a change in EHT (Δt_e ; t_e is effective hydration temperature) produces a change in rim value (Δr):

$$\Delta r/r = -\frac{1}{2} (E/RT_e^2) \Delta t_e \quad (9)$$

For $E = 20$ KJ/mol and 90 KJ/mol, Eq. (9) gives 0.0140 and 0.0630, respectively, with a median E value of 0.0007 per KJ/mol. The former leads to a change in rim of about 1–6 %/ $^\circ\text{C}$, and the higher holds for nominal conditions. A cautionary note is that the meteorological data are for air temperatures, while obsidian usually is found at a variable depth in the ground where T differs. Alternatively, sensors (e.g., HOBO H8 Family loggers, e.g., Stevenson et al. 2013) are put over a year in situ that record a meaningful annual context meteorological average.

Rim

Typically, the mean and standard deviation of an aggregate of about six individual readings is taken for each hydration rim measurement reported by a laboratory. Standard deviations are nearly always $<0.1\text{ }\mu\text{m}$, more often $0.05\text{--}0.01\text{ }\mu\text{m}$. A previous analysis (Scheetz and Stevenson 1988) concluded that the accuracy is constrained by the resolution of the microscope system to $\sim 0.25\text{ }\mu\text{m}$ or worse; however, the issue here is not resolution but accuracy of coincidence measurement, which is well known to be about two orders of magnitude better than resolution (Jacobs 1943, pp. 86–88), so the error values quoted by obsidian laboratories are reasonable but the precision weak as recent methods have shown. A comparison of optical readings with hydrogen profiles collected by SIMS (Anovitz et al. 1999; Stevenson et al. 2001) and infrared profiling (Yokoyama et al. 2008) show that the depth of water diffusion extends well beyond the optically defined diffusion front. As a result, optical techniques cannot accurately track the diffused species. SIMS has been used to significantly increase precision to $\pm 0.05\text{--}0.1\text{ }\mu\text{m}$, but the cost per sample is prohibitive for routine application.

Higher precision of the rim reading is achieved by SIMS profiles or IR-PAS peak integration (Anovitz et al. 1999; Stevenson et al. 2001, 2002).

Diffusion Rate, D

Simulation experiments of hydration rate by laboratory methods (sometimes known as “induced hydration”) have an equivocal history in archaeology, and since it depends on temperature, attempts have been made in the past to measure hydration rate in the laboratory (e.g., Friedman and Long 1976; Stevenson et al. 1998). However, rates measured in the laboratory often have not agreed well with archaeological data (see, e.g., the pointed observations in Hall and Jackson 1989, p. 32), while in other cases agree (e.g., for Rapa Nui Easter Island, Stevenson et al. (2013) and in Topaz Mountain obsidian from Utah, Rogers and Duke (2011)). The hydration rate of obsidian, which is strongly temperature dependent, is allowed to proceed at elevated laboratory temperatures, when measurable hydration rims develop in days rather than years. The temperature dependence of the hydration rate has a well-attested mathematical form, so the principle of laboratory hydration is to hydrate a set of obsidian samples at elevated temperatures, determine the activation energy and diffusion constant, and then compute the hydration rate for temperatures of archaeological interest. Initially, the diffusion rate D was calculated from hydration that was experimentally induced under controlled laboratory experiments for use in the Arrhenius plot, in a high temperature range ($90\text{--}250\text{ }^{\circ}\text{C}$) (Stevenson et al. 1998). First, this did not secure safe extrapolation to much lower temperatures, and second, the simulated hydration does not produce the anticipated behavior with obsidian of similar source. Making use of nano-SIMS and simulation experiments, rates are produced at environmental conditions. Such an aging experiment for Papua New Guinea obsidians has shown differing diffusion rates for the same temperature and different storage temperatures of four different sources. There, the SIMS profile depths and regression results for the four hydrated obsidians, namely, Igwageta, Mt Bao, Wekwok, and Umleang, produced diffusion rates that vary by $\sim \times 25$ for a fourfold temperature increase, between $10\text{ }^{\circ}\text{C}$ ($0.002\text{--}0.004$) and $40\text{ }^{\circ}\text{C}$ ($0.06\text{--}0.10$) for the four different sources, which, however, have no marked chemical composition variation (Ambrose and Novak 2012). From room temperature to $75\text{ }^{\circ}\text{C}$, the diffusion coefficient changes by two to three orders of magnitude confirming the well-known sensitivity of the intrinsic dating technique to assumed local temperature (Anovitz et al. 2004).

This had resulted in high measurement error stemming from the use of optical methods; thus, the regression constants also had a large inherent error. But, data have shown a relationship between structural water concentration and D , and an increase in precision is now achieved through the

analysis using infrared measurement of experimentally developed hydration layers (Stevenson et al. 2001).

The errors and their affects have been exhaustively analyzed (Rogers 2010). Hydration rates can be reliably estimated by least squares techniques applied to obsidian-radiocarbon data with errors of about 4–5 %, while rates estimated by least squares techniques applied to time-sensitive artifacts are somewhat worse, with about 8–10 % errors. Rates determined from laboratory techniques (induced hydration) are somewhat more accurate, with about 2–3 % error.

Analytical errors concern (a) the mathematical procedure of a least squares best fit to the logarithmic Arrhenius equation (see Stevenson and Scheetz 1989; Rogers and Duke 2011), especially if data-point weighting is not included (otherwise the activation energy and diffusion constant will be in error); (b) the procedural error that involves laboratory techniques (e.g., erosion rates and rim growth, use of proper hydration environment and temperature); (c) the “scaling” problem, i.e., hydration at high lab temperatures and archaeological temperatures (the scaling is actually a complex function of the both hydration rates (and diffusion constant) and their activation energies and requires knowledge of both for each obsidian source in question); and last, but not least, (d) the role of phenocrysts presence (size and abundance) and obsidian transparency should also be reexamined for they obviate ideal diffusion process.

The Dependence of Time

The dependence of time on the square exponent of x has been questioned (Anovitz et al. 1999, 2004; Liritzis 2006). That is why most reported OHD ages are compared with other dating means (^{14}C , luminescence, ceramic typology), an expected practice for the initial development of the method, though in several cases the square root is valid.

The Surface Loss

The surface loss is identified as an important factor in glass hydration dating (Ambrose 1976, 1994; Liritzis et al. 2008a, b; Morganstein et al. 1999). Once present on an artifact with fissures, the surface dissolution rate of an obsidian artifact can be calculated. Although OHD theoretically is capable of yielding accurate dates in the range 1,000,000 to 200 years B.P. (Michels 1986), the obsidian surface is subjected to environmental flaking, and this limits its range; on the other hand, the nano-SIMS technology at least provides an accurate minimal rim reading that can deal with this issue.

Humidity

Humidity effects are relatively small and are typically ignored in analysis. However, the effect of accelerated hydrations with 100 % Rh on diffusion kinetics has not been adequately studied.

Intrinsic (Pristine or Connate) Water

The remaining variable hydration associated with original fast cooling of lava is an extremely important factor in the diffusion rate. The hydration rate in obsidian at any given temperature is a function of the concentration of water in the glass (Karsten and Delaney 1981; Karsten et al. 1982; Stevenson et al. 1998; Zhang and Behrens 2000; Zhang et al. 1991). Intra-source variability in intrinsic water content has been observed in Coso obsidians from eastern California, USA (Stevenson et al. 1993), and is likely present in others; thus, measurement of intrinsic water content per individual specimen is required as a prerequisite (Stevenson et al. 2001, 2002).

Some Early and Recent OHD Applications and Development

Friedman et al. (1997) provided a substantive review and summarized the problems linked to OHD and referred to case studies including archaeological specimens from New Mexico, central Mexico, Belize, Honduras, and Ohio (the latter imported from Wyoming). Studies of Mexican, Guatemalan, and Sardinian obsidians by Michels and his colleagues however are critiqued therein. The authors cross-dated OHD results with radiocarbon dating, archaeomagnetism, and ceramic phasing. Particular points to take care of included the factors related to hydration rates (as chemical composition of obsidians, their trace elements content, relative humidity, and regional rates), laboratory techniques (preparation of thin sections, optical measurement of hydration rim/rind thickness), and the conversion of hydration rate data to age. In their review, OHD was however promoted as a relatively inexpensive and “simple” scientific technique for determining absolute chronologies, so that the current masterful treatments presented replaced the earlier general assessment.

A series of OHD dates was reported consecutively by the UCLA laboratory (see Meighan and Scalise 1988).

Braswell (1992) pointed out problems concerning laboratory determinations of diffusion rate constants and the estimation of EHT in the field, from a study of the Coner Phase at Copas (Honduras). He concluded that the laboratory-induced rate constants used to determine these dates were of questionable validity and needed to be independently assessed. He showed how an error of but a few Kelvin in estimated EHT can lead to dates that are in error by several centuries. In view of the likelihood of large errors in the Copán obsidian dates, the assertion that the Late Classic Coner phase should be extended beyond 900 A.D. was considered therefore premature (Braswell 1992; Webster and Freter 1990)

Further application in OHD includes the dating of New Zealand obsidians by Stevenson et al. (1996), with a recent age span from 13th to 18th A.D., where hydration rates were calculated on the basis of obsidian water content as estimated from artifact density, while effective hydration temperatures were established from published temperatures derived from thermal cells. The deduced hydration dates have been successfully compared with radiocarbon dates from six archaeological sites in the North Island of New Zealand.

Ambrose (1994) gave a provisional age-depth model for hydration thicknesses for the Pamwak site, Manus Island, Papua New Guinea, spanning from 4 to 13 ka BP, based on internal crack surfaces and compared satisfactorily with ^{14}C age control.

Obsidian hydration dating has served as one of the chronological indicators for the Hopewell Culture earthworks (ca. 200 B.C.–A.D. 500) in central Ohio (Stevenson et al. 2004). This work presented new obsidian hydration dates developed from high precision hydration layer depth profiling using SIMS, and the data suggested that long-distance exchange in obsidian occurred throughout the Hopewell period. From Eq. (2) parameters, diffusion coefficient A and activation energy E were estimated by the density versus OH^- plot; EHT from cell pairs put in the site and Eq. (2) resulted in OHD age estimates that range between 258 and 119 B.C. and A.D. 607–94, and these incorporate the entire Hopewell period, as determined by absolute C-14 dates of the same site.

Based upon the water diffusion in natural glass, Stevenson et al. (2007) introduced the conventional OHD technique to dating high-calcium manufactured glasses with first preliminary results on seventeenth-century North American glass wine bottles manufactured by European settlers, concordant with historical data.

In many cases, intact internal fissures as concealed cracks can be used for OHD, and the rate of surface loss can be calculated from paired readings of these inner surfaces and the outer weathered

(depleted) ones (Ambrose 1998). When secondary rate factors for these fissures were compared to radiocarbon-based rates, a discrepancy was found due to dissolution.

At any rate, since OHD is dependent on processes which have occurred since an artifact was created, it can never be as accurate and reliable as radiocarbon or dendrochronology, and it should be always a secondary source of chronological data. Thus, in this frame, using a radiocarbon assay remains the basis for relative hydration dating; but this raises again the question, for a given site, of the true association of the artifact and the ^{14}C date and, for nearby sites, the remaining uncertainty of the validity of the constancy of environmental characteristics.

The ongoing Easter Island OHD by Stevenson et al. (2011) with more than 800 obsidian specimens analyzed has been advanced with the IR-PAS measurements of D and water, and ages are comparable to ^{14}C ones in the time span of fourteenth to nineteenth century A.D.

SIMS-SS has been applied to obsidians from several parts of the world (e.g., Greece, Chile, Turkey, Japan, Hungary, the USA) with ages from a few hundred to 30,000 years BP (Liritzis and Laskaris 2009, 2012).

Analysis of errors shows that it is unrealistic to expect age errors much less than 15–20 % in obsidian hydration dating (Rogers 2010). With those uncertainties in the computed ages, great caution must be exerted in inferring occupation duration of a site used based on OHD.

Conclusion

The process of hydration in glasses is very complex, involving chemistry, physics, and mathematical modeling. Obsidian hydration has certain weaknesses in terms of a chronometric tool like any other dating method. At any rate, two fundamental equations involved need further experimentation or prior calibration: an age equation of classical OHD and a temperature dependence equation, which is usually of the Arrhenius form and the SIMS-SS. Since the transport parameters being measured differ, the age equations differ slightly as well, in particular the exponent of the time (age) variable. It is likely that the parameters of the Arrhenius equation are slightly different as well, although investigations of this point have not yet been reported. However, it would be unwise to apply, say, an activation energy determined from water mass uptake to the optical (classical OHD) case without careful study or EHT and hydration experiments at ambient conditions.

Despite the fact that the classical OHD is furthest removed from the basic physics of hydration (criticism by advocates of other techniques, e.g., Anovitz et al. 1999; Liritzis and Laskaris 2012), it is still being used since it seems to satisfy coarse chronologies especially of recent centuries, whereas other chronometric data are frequently lacking (Stevenson et al. 2013). The alternative SIMS-SS with the mathematical techniques discussed also offers satisfactory dates for the past 30,000 years (Liritzis and Laskaris 2009, 2011, 2012).

Probably, the greatest needs at present are for (1) a more scientific approach of the age equation; (2) more dates on a “join forces” basis, for the two current approaches, for specimens throughout the world, and comparison with luminescence and C-14; and (3) development of not expensive versions of OHD.

Cross-References

- [Luminescence, Flints and Stones](#)
- [Luminescence Dating](#)
- [Radiocarbon, Plant Materials](#)

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URL

http://www.obsidianlab.com/info_oh.html

<http://www.rhodes.aegean.gr/tms/sims-ss/index.html>

Ar–Ar and K–Ar Dating

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Synonyms

(Argon–argon): Ar–Ar, ^{40}Ar – ^{39}Ar , $^{40}\text{Ar}/^{39}\text{Ar}$, ^{39}Ar – ^{40}Ar , $^{39}\text{Ar}/^{40}\text{Ar}$, argon-40/argon-39;
(Potassium–argon): K–Ar, ^{40}K – ^{40}Ar , ^{40}Ar – ^{40}K

Definition

Potassium–argon dating. An absolute dating method based on the natural radioactive decay of ^{40}K to ^{40}Ar used to determine the ages of rocks and minerals on geological time scales.

Argon–argon dating. A variant of the K–Ar dating method fundamentally based on the natural radioactive decay of ^{40}K to ^{40}Ar , but which uses an artificially generated isotope of argon (^{39}Ar) (produced through the neutron irradiation of naturally occurring ^{39}K) as a proxy for ^{40}K .

K–Ar Dating

The potassium–argon (K–Ar) geochronological method is one of the oldest absolute dating methods and is based upon the occurrence of a radioactive isotope of potassium (^{40}K), which naturally decays to a stable daughter isotope of argon (radiogenic ^{40}Ar , also known as $^{40}\text{Ar}^*$). For this reason, the K–Ar method is one of the few radiometric dating techniques in which the parent (^{40}K , a solid) is a different phase from the daughter (^{40}Ar , a gas). The method was first suggested by Goodman and Evans (1941) and one of the earliest K–Ar ages was published by Smits and Gentner (1950). Because potassium is a major or minor element in many minerals, the K–Ar dating technique has been used to date a diverse range of rock types. A comprehensive and detailed overview of the method can be found in Dalrymple and Lanphere (1969).

The conventional K–Ar method became widely used soon after its development and can give reliable ages on many rapidly cooled rocks (e.g., volcanics, dykes). There are, however, a number of limitations with respect to the interpretation of K–Ar ages (further discussed below) which has led to a very limited use of the K–Ar method in current studies. These limitations are largely overcome by the Ar–Ar method, however, which has now superseded the K–Ar method as the geochronological method of choice in dating K-bearing minerals and is further described below.

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Types of Materials Which Can Be Dated

Any potassium-bearing solid material has the potential to be dated by either the K–Ar or Ar–Ar methods. Because many common rock-forming minerals contain K, the Ar–Ar method is one of the most commonly employed geochronological techniques in many geological studies. The most common materials that are particularly well suited to dating using the K–Ar or Ar–Ar technique include:

K-feldspar	Biotite	Phlogopite	Glasses (e.g., tektites)
Plagioclase	Muscovite	Nepheline	Clays and slates
Hornblende	Sericite	Alunite	Basalts

In general, it should be noted that pure, unaltered minerals yield the best results.

Clays and materials composed of very small grains can be problematic in Ar–Ar dating, depending on their grain size. If the grain size is smaller than about 1 μm , an experimental effect known as “ ^{39}Ar recoil” associated with the neutron irradiation of the sample can make the interpretation of the results difficult; this is further discussed below. For this reason, K–Ar dating may remain the preferred method of dating clays and very fine-grained K-bearing minerals.

Natural Isotopic Abundances

Potassium has three naturally occurring isotopes with the following natural abundances: ^{39}K (93.2581 %), ^{40}K (0.01167 %), and ^{41}K (6.7302 %) (Steiger and Jäger 1977). Of these three isotopes, only ^{40}K is radioactive.

Argon also has three naturally occurring isotopes with the following natural abundances: ^{36}Ar (0.337 %), ^{38}Ar (0.063 %), and ^{40}Ar (99.6 %) (Nier 1950; Steiger and Jäger 1977). Although all three isotopes are stable, ^{40}Ar is the only isotope that is also a radiogenic daughter product (resulting from the decay of ^{40}K). From these abundances, the atmospheric ratio of $^{40}\text{Ar}/^{36}\text{Ar}$ [often denoted as $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{a}}$] is thus 295.5. This ratio is required in the calculation of ^{40}Ar – ^{39}Ar ages, as explained below.

Radioactive Decay Scheme

The K–Ar method is unique among geochronological schemes because the radioactive parent (^{40}K) undergoes a complex branched radioactive decay to both radiogenic ^{40}Ca and ^{40}Ar (Fig. 1).

The dominant mode of decay (89.5 % of the time) is the emission of a β -particle leading to the formation of radiogenic ^{40}Ca . However, ^{40}K can also decay via one of three other modes to radiogenic ^{40}Ar . The most common mode is via electron capture; this may result in the formation of ^{40}Ar in an excited state that subsequently drops to the ground state with the additional release of a γ -ray (10.3 % of the time) or, less commonly, may directly form at the ground state (0.16 % of the time). A very rare mode of decay to ^{40}Ar (only 0.001 % of the time) resulting from the emission of a positron (β^+) has also been hypothesized.

The most widely used set of decay constants for ^{40}K is published by Steiger and Jäger (1977): $\lambda_{\beta^-} = 4.962 \times 10^{-10} \text{ a}^{-1}$ and $\lambda_{\text{e}} + \lambda_{\beta^+}$ (all other branches combined) = $0.581 \times 10^{-10} \text{ a}^{-1}$ for a total decay constant of $\lambda = 5.543 \times 10^{-10} \text{ a}^{-1}$. Thus, the corresponding half-life of ^{40}K is $\ln 2/\lambda = 1,250 \text{ Ma}$.

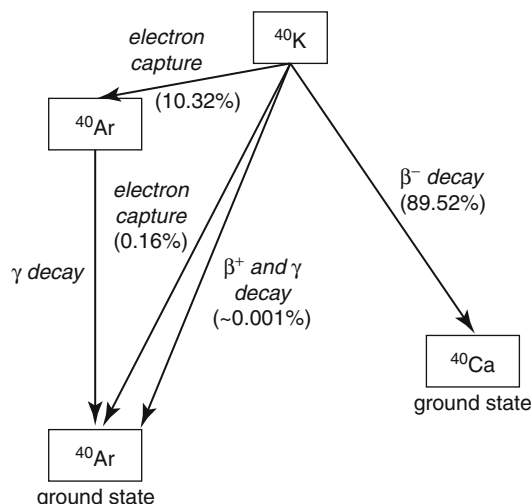


Fig. 1 ^{40}K decay scheme (After McDougall and Harrison 1999), based on the decay constants of Steiger and Jäger (1977)

High-resolution geochronological studies integrating data from different isotopic systems (e.g., the timing of mass extinctions, the geological time scale) have generated widespread renewed interest throughout the geochronological community in the accuracy and precision of the ^{40}K decay constants ($\lambda = \lambda_e + \lambda_\beta$) due to the existence of small but statistically significant age discrepancies of same precisely dated events by the K–Ar and U–Pb systems. Renne et al. (1998) first noted an ~2.1 % discrepancy between the value of λ_e used by geologists and that used by nuclear physicists – a potential source of systematic error. Min et al. (2000) statistically evaluated the nuclear physics database as well as estimated the total decay constant λ as calibrated with U–Pb and historical dating; their findings led them to suggest tentative values for λ which differ from the currently used value by –1.4 % to –3.1 %, leading to an international call for an improved set of all geochronological decay constants (Begemann et al. 2001). After a careful intercalibration of the widely used Fish Canyon sanidine (FCs) standard with primary K–Ar standards, Jourdan and Renne (2007) stated that there was an imminent need for the revision of the ^{40}K decay constant λ , particularly in the electron-capture branch (i.e., to ^{40}Ar). Kuiper et al. (2008) published a unique study indirectly recalibrating λ by dating sanidine from very precisely dated, astronomically tuned ash beds; their revised estimate of λ brings into synchronicity the Ar–Ar and U–Pb ages of a number of globally significant geological events (e.g., K–T and P–Tr boundaries). Recently, Renne et al. (2010) used a Monte Carlo optimization methodology of all available ^{40}K activity data and integrated ^{238}U – ^{206}Pb and ^{40}Ar – ^{39}Ar data pairs to estimate an optimal λ and corresponding uncertainties. Despite these advances, however, a common set of updated K decay constants has yet to be agreed upon and adopted by the global scientific community.

K–Ar Age Equation

From first principles, it can be shown that the K–Ar age equation is

$$t = \frac{1}{\lambda} \ln \left(\frac{\lambda}{\lambda_e} \cdot \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}} + 1 \right) \quad (1)$$

where $t = \text{age}$, $\lambda_e = 0.581 \times 10^{-10} \text{ a}^{-1}$, $\lambda = 5.543 \times 10^{-10} \text{ a}^{-1}$, and ^{40}K and $^{40}\text{Ar}^*$ are the number of atoms (e.g., moles) of each element, respectively. Note that the asterisk (*) in $^{40}\text{Ar}^*$ is used by convention in the literature to denote radiogenic ^{40}Ar (i.e., derived from the radioactive decay of ^{40}K in the same sample), as opposed to ^{40}Ar from other sources, such as the atmosphere (often denoted as $^{40}\text{Ar}_a$) or excess Ar from the Earth's crust or mantle (sometimes denoted as $^{40}\text{Ar}_E$).

Thus, in order to calculate a K–Ar age [which is directly proportional to the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio according to Eq. (1)], one must determine both the $^{40}\text{Ar}^*$ and ^{40}K in the sample.

Ar–Ar Dating

Ar–Ar dating was introduced in the mid-1960s, with the publication of a landmark paper by Merrihue and Turner (1966). The most comprehensive and detailed overview of all aspects of the method can be found in McDougall and Harrison (1999) although some of the data interpretation sections tend to reflect author biases. Dickin (2005) also provides a more concise summary of the technique.

The Ar–Ar method is fundamentally based on the K–Ar method. However, instead of directly measuring ^{40}K , the sample is placed in a nuclear reactor and bombarded with fast neutrons (having energies $>0.1 \text{ MeV}$) to transform a proportion of the potassium (specifically, the fraction associated with ^{39}K) to another isotope of argon, ^{39}Ar . The process results in the addition of the neutron (n) to the ^{39}K nucleus, resulting in the ejection of a proton (p) and energy in a process that can be summarized as follows:



Equation (2) can also be written in the abbreviated form $^{39}\text{K}(n, p)^{39}\text{Ar}$. ^{39}Ar produced in this way is commonly designated as $^{39}\text{Ar}_K$ denoting the fact that it was derived from the neutron irradiation of K. Because $^{39}\text{Ar}_K$ is not a naturally occurring argon isotope, it is directly proportional to the amount of ^{39}K (and hence ^{40}K , because the natural abundances of the K isotopes are known, i.e., the ^{39}K – ^{40}K ratio is known and constant, as stated above) in the sample. Thus, ^{39}Ar serves as an effective proxy for ^{40}K (and therefore, the $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ ratio is directly proportional to the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio).

Ar–Ar Age Equation

The $^{40}\text{Ar}/^{39}\text{Ar}_K$ ratio cannot be directly substituted for the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio in Eq. (1) because the amount of ^{39}Ar generated from the neutron irradiation will clearly be a function of the amount of ^{39}K in the sample, the duration of the irradiation, the neutron flux, and the proportion of fast neutrons within the neutron flux, i.e.,

$$^{39}\text{Ar}_K = ^{39}\text{K} \Delta \int_E \phi(E) \sigma(E) dE = ^{40}\text{K} \left(\frac{^{39}\text{K}}{^{40}\text{K}} \right)_{ab} \Delta \int_E \phi(E) \sigma(E) dE \quad (3)$$

where Δ is the duration of the irradiation, $\phi(E)$ is the neutron flux at energy E , $\sigma(E)$ is the neutron

capture cross section at energy E for the conversion reaction described in Eq. (2), and $(^{39}\text{K}-^{40}\text{K})_{\text{ab}}$ is the $^{39}\text{K}-^{40}\text{K}$ ratio from the natural atomic abundances.

Substitution of Eq. (3) into Eq. (1) thus yields

$$t = \frac{1}{\lambda} \ln \left(\frac{\lambda}{\lambda_e} \cdot \frac{{}^{40}\text{Ar}^*}{{}^{39}\text{Ar}_{\text{K}}} \left[\left(\frac{{}^{39}\text{K}}{{}^{40}\text{K}} \right)_{\text{ab}} \Delta \int_E \phi(E) \sigma(E) dE \right] + 1 \right) \quad (4)$$

The determination of the neutron irradiation parameters in Eq. (4) is not trivial and will vary for each irradiation. Therefore, the Ar–Ar age determination can be greatly simplified if an age standard (sometimes called a monitor mineral) is used. If the age of the standard is known (designated as t_s), then Eq. (4) becomes

$$t_s = \frac{1}{\lambda} \ln \left\{ \frac{\lambda}{\lambda_e} \cdot \left(\frac{{}^{40}\text{Ar}^*}{{}^{39}\text{Ar}_{\text{K}}} \right)_s \left[\left(\frac{{}^{39}\text{K}}{{}^{40}\text{K}} \right)_{\text{ab}} \Delta \int_E \phi(E) \sigma(E) dE \right] + 1 \right\} \quad (5)$$

Common practice is to gather all of the constant terms to define an irradiation parameter J , where

$$J = \frac{\lambda}{\lambda_e} \cdot \left(\frac{{}^{39}\text{K}}{{}^{40}\text{K}} \right)_{\text{ab}} \Delta \int_E \phi(E) \sigma(E) dE \quad (6)$$

so that substitution into Eq. (5) yields

$$t_s = \frac{1}{\lambda} \ln \left\{ J \left(\frac{{}^{40}\text{Ar}^*}{{}^{39}\text{Ar}_{\text{K}}} \right)_s + 1 \right\} \quad (7)$$

or rearranging,

$$J = \frac{e^{\lambda t_s} - 1}{({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{\text{K}})_s} = \frac{e^{\lambda t_u} - 1}{({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{\text{K}})_u} \quad (8)$$

However, for a sample of unknown age (herein designated by the subscript u), we obtain from Eq. (7) an analogous age equation for the unknown:

$$t_u = \frac{1}{\lambda} \ln \left\{ J \left(\frac{{}^{40}\text{Ar}^*}{{}^{39}\text{Ar}_{\text{K}}} \right)_u + 1 \right\} \quad (9)$$

Thus, by substituting Eq. (8) into Eq. (9), we obtain the Ar–Ar age equation:

$$t_u = \frac{1}{\lambda} \ln \left\{ \frac{({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{\text{K}})_u}{({}^{40}\text{Ar}^*/{}^{39}\text{Ar}_{\text{K}})_s} (e^{\lambda t_s} - 1) + 1 \right\} \quad (10)$$

This equation can be compared with the K–Ar age equation [Eq.(1)]. Significantly, this shows that an age standard must always be irradiated with an unknown sample.

Sample Preparation

Sample preparation for both K–Ar and Ar–Ar dating is generally similar. In both cases, the most important criterion is the use of fresh, unaltered samples which are free of inclusions or other contaminants. Also, it is essential to know the geological context of the minerals to be dated so thin-section petrography of the sample to be dated should be the first step. Where aliquots of a mineral are required, rock samples are usually crushed to the grain size of the minerals to be dated. After sieving and ultrasonic washing in acetone and distilled water, mineral separates are obtained through standard techniques, such as the use of magnetic separators or heavy liquids. Ultrapure mineral separates are required because even a small amount of impurities or other minerals can contaminate an argon analysis. As a result, mineral separates are usually inspected carefully under a binocular microscope and only pristine grains (i.e., free from inclusions, defects, or other mineral contaminants) are retained. In this way, mineral separates with >99.9 % purity can be obtained.

The application of lasers in Ar–Ar dating has greatly simplified the sample preparation process. Because much less sample is required, e.g., single crystals are often analyzed, mineral separation can be relatively quick. Furthermore, the use of lasers as age microprobes has allowed the analysis of minerals in situ, typically in a polished thick (100–200 μm) section.

In Ar–Ar dating, the samples to be dated (either single crystals, aliquots of crystals, or a thick section) are commonly wrapped in Al foil or encapsulated in silica tubes, along with the age standard, and then irradiated in a nuclear reactor. The age of a suitable standard and the optimum duration of irradiation should all be carefully considered at this stage. More details can be found in McDougall and Harrison (1999).

Analytical Methods

The following is a general summary of the analytical methods employed in both K–Ar and Ar–Ar dating. Detailed descriptions of the methodology for each dating technique can be found in Dalrymple and Lanphere (1969) and McDougall and Harrison (1999), respectively.

Potassium

The analysis of potassium typically involves wet-chemical or physical methods.

Most K–Ar studies in the early literature employed the use of flame photometry to determine K concentration, which is based on the fact that all elements emit characteristic photons when excited electrons drop back to their ground state. In general, the rock or mineral is dissolved in acid and unwanted elements (such as Si) are removed through a variety of chemical reactions. By heating the potassium-enriched solution with a gas–air flame, measurement of the distinct photon wavelengths emitted by the excited electrons will distinguish the various elements, and the measurement of the intensity of the radiation is directly proportional to the amount of the element in the sample. Unknown samples are calibrated by also analyzing standard solutions of various (known) potassium concentrations and by adding an internal alkali metal standard (typically Li) to the unknown solution. Uncertainties are typically on the order of ± 1 %.

Other analytical methods that have been used less frequently to measure K concentrations include atomic absorption spectroscopy, based on the absorption of radiant energy by potassium atoms, which produce an absorption spectrum characteristic of that element; X-ray fluorescence, based on the X-ray emission spectrum of potassium resulting from bombarding the sample with an X-ray beam; neutron activation, in which an artificial unstable isotope of K (^{42}K) is created by irradiating

the sample with neutrons to convert ^{41}K and its subsequent γ -decay is measured; and isotope dilution, in which a known quantity of an isotopic tracer (known as a “spike,” typically ^{41}K) is added to the unknown solution before measuring all of the K isotopes in a solid-source mass spectrometer.

Argon

Argon in both K–Ar and Ar–Ar dating is measured in a two-step process typically involving extraction and purification from the mineral sample and then measurement and calculation of the $^{40}\text{Ar}^*$. Because argon is a gas, the easiest way to extract argon is to fuse the sample at high temperature. This is usually done in a high-vacuum system using a radio-frequency (induction) or resistance furnace or a laser (in Ar–Ar dating only). Because other gases, such as N_2 , O_2 , or CO_2 , can also be released, the argon is purified through the use of liquid nitrogen traps, Zr-alloy getters, and Ti sponges. The purified argon is then analyzed in an ultrahigh vacuum system in a noble gas mass spectrometer. Simply, the argon that enters the mass spectrometer is first ionized in the ion source. The resultant beam of positive Ar ions is collimated and then accelerated through both electric and magnetic fields that separate the beam into a series of beams that follow a curved flight path, each with a distinct charge/mass ratio. Older mass spectrometers had only a single detector to measure the incoming beam current (proportional to the number of Ar atoms), but latest-generation mass spectrometers now have multicollector capability.

In K–Ar dating, because $^{40}\text{Ar}^*$ and ^{40}K must be measured separately, a method is required to determine the absolute concentration of $^{40}\text{Ar}^*$ in the unknown sample. The most widely used method is by isotope dilution. In this method, a known quantity of an argon tracer (also called a “spike”) is mixed with the argon from the unknown sample. The distinguishing characteristic of the spike is that it must have a known argon isotopic composition, i.e., the ratio of ^{36}Ar – ^{38}Ar – ^{40}Ar , different to the natural abundance of these isotopes. Since the isotopic composition of the mixture can be measured in the mass spectrometer and the argon isotopic composition and amount of spike are known, it is then possible to calculate the isotopic composition and amount of the argon from the unknown. Argon tracers are typically enriched in ^{38}Ar , and all three naturally occurring argon isotopes (^{36}Ar , ^{38}Ar , and ^{40}Ar) are measured in the mass spectrometer. Dalrymple and Lanphere (1969) describe the isotope dilution process in more detail.

In Ar–Ar dating, only the ratio of two argon isotopes ($^{40}\text{Ar}^*$ and $^{39}\text{Ar}_\text{K}$) is required in the age equation [Eq. (10)], so the argon analysis is, in principle, much simpler than in K–Ar dating because absolute concentrations are not required. However, because of neutron-induced interference reactions (described below), five argon isotopes (^{36}Ar , ^{37}Ar , ^{38}Ar , ^{39}Ar , and ^{40}Ar) must be measured.

Data Corrections

There are several important corrections that must be applied to the raw data in order to calculate an accurate age.

Blank Correction

Although argon is measured in an ultrahigh vacuum environment in both K–Ar and Ar–Ar dating, system blanks from both the extraction line and mass spectrometer must be subtracted from the total amount of each argon isotope measured.

Atmospheric Correction

This is the most fundamental correction in both K–Ar and Ar–Ar dating. Because ^{40}Ar is the most abundant isotope of argon in the atmosphere, it can be adsorbed onto the surface of mineral grains or analytical equipment or can be incorporated into minerals during crystallization, so a correction must be made to subtract this atmospheric component ($^{40}\text{Ar}_a$) from the total amount of ^{40}Ar measured. Since it is impossible to distinguish $^{40}\text{Ar}_a$ from $^{40}\text{Ar}^*$, another isotope of argon present in the atmosphere ($^{36}\text{Ar}_a$) is also measured in the mass spectrometer. Since the atmospheric ratio ($^{40}\text{Ar}/^{36}\text{Ar}$)_a is 295.5, the atmospheric ^{40}Ar component is easily calculated as $^{40}\text{Ar}_a = 295.5 \times ^{36}\text{Ar}_a$. Depending on the age of the sample or the amount of gas being measured, this correction can be significant, e.g., for young samples or samples with very low K.

Neutron-Induced Interferences

In Ar–Ar dating, neutron bombardment of most minerals generates numerous reactions with elements other than K that produce a variety of argon isotopes. These neutron-induced interferences must therefore be corrected in order to obtain accurate ages. The most important reactions are [cf. Eq. (2)] $^{40}\text{Ca}(n, n\alpha)^{36}\text{Ar}$, $^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}$ (^{37}Ar is radioactive and decays to ^{37}Cl with a half-life of 35.1 days), $^{37}\text{Cl}(n, \gamma)^{38}\text{Cl} \rightarrow ^{38}\text{Ar}$ (^{38}Cl is radioactive and decays to ^{38}Ar with a half-life of 37.3 min), $^{42}\text{Ca}(n, \alpha)^{39}\text{Ar}$, $^{39}\text{K}(n, p)^{39}\text{Ar}$, and $^{40}\text{K}(n, p)^{40}\text{Ar}$. From these reactions, it can be seen that neutron-induced interferences will affect the measurement of five argon isotopes (^{36}Ar , ^{37}Ar , ^{38}Ar , ^{39}Ar , and ^{40}Ar) and are the reason why all of these isotopes must be measured. McDougall and Harrison (1999) describe in detail the added complexities in the data correction process resulting from neutron irradiation in Ar–Ar dating.

Radioactive Decay Correction

In Ar–Ar dating, two of the artificial argon isotopes produced by neutron irradiation ($^{37}\text{Ar}_{\text{Ca}}$ and $^{39}\text{Ar}_{\text{K}}$) are themselves radioactive with half-lives that are on a time scale of days to years. $^{37}\text{Ar}_{\text{Ca}}$ has a half-life of about 35.1 days and $^{39}\text{Ar}_{\text{K}}$ has a half-life of 269 years (Stoerner et al. 1965), so further corrections for the time interval between neutron irradiation and analysis in the laboratory must also be made.

Modes of Analysis

Conventional (Total Fusion) Age

The analysis of a sample in conventional K–Ar dating produces a single age, since the sample must be completely dissolved and fused in order to extract the ^{40}K and ^{40}Ar , respectively. The analogous process (total fusion) can be performed in the Ar–Ar analysis of a sample to yield a single, total fusion age. Because of the decreased sensitivity of early-generation mass spectrometers, several milligrams of purified mineral separates often had to be analyzed to obtain enough argon to calculate an age. Improved sensitivity of current-generation mass spectrometers now permits the Ar–Ar analysis of single crystals which can be fused with either a furnace or a laser. In fact, lasers can be used as age microprobes to obtain intragrain Ar–Ar age analyses, in which a small amount of material can be ablated by the laser within a mineral grain and yields a total fusion age for that spot. Ar–Ar laser microprobes thus permit the direct determination of the ^{40}Ar (age) distribution within single crystals. For more information about single-crystal laser dating, see the entry “► [Single-Crystal Laser Fusion](#).”

Ar–Ar Step-Heating

Because the Ar–Ar method only requires the extraction of gaseous argon isotopes, Merrihue and Turner (1966) noted that the sample did not have to be fused in a single step, but could be incrementally heated in steps of increasing temperature, and the argon isotopes extracted during each temperature step could be analyzed to yield an age for that step. This incremental-heating (or step-heating) technique thus was a major advantage over conventional K–Ar dating because it provided a way to examine the distribution of ^{40}Ar (and hence, ages) within minerals. The fundamental principle is based on solid-state diffusion theory and is illustrated in Fig. 2.

Consider a homogeneous spherical mineral grain. If the grain is heated at a relatively low temperature (T_1) for a finite period of time, the argon isotopes diffusing out of the grain can only come from a thin region (i.e., shell) along the boundary of the grain and will yield an age t_1 associated with that region. If the grain is now heated at a slightly higher temperature (e.g., $T_2 > T_1$) for the same length of time, the argon isotopes will diffuse from a spherical region that extends slightly deeper into the grain and will yield an age t_2 . In this way, successively higher steps of increasing T will sample regions deeper and deeper into the grain until the highest temperature steps (e.g., T_9) will sample the argon from the grain core. The age of each step is commonly referred to as an apparent age because it may not necessarily be identical to the overall age of the mineral grain.

By plotting the apparent ages of each of the steps (t_1 – t_9) in a diagram of apparent age versus the cumulative fraction of $^{39}\text{Ar}_\text{K}$ released, a so-called apparent age spectrum can be constructed. For example, consider the same spherical grain in Fig. 2. If ^{39}K is homogeneous throughout the grain (i.e., K is not chemically zoned), then the $^{39}\text{Ar}_\text{K}$ produced from the fast-neutron irradiation of the ^{39}K should also be uniformly distributed throughout the grain from core to rim. If the ^{40}Ar distribution is uniform throughout the grain, then ^{40}Ar – $^{39}\text{Ar}_\text{K}$ ratio (and thus, apparent age) should be identical for every step (t_1 – t_9) and the resultant apparent age spectrum yields a “plateau” age (Fig. 3). The significance of a plateau age is discussed in the following section.

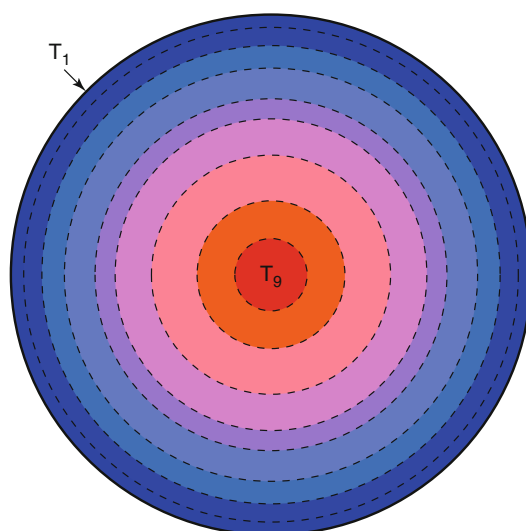


Fig. 2 Hypothetical spherical grain subject to step-heating. By heating the grain in incremental steps of increasing temperature, argon (and hence, the age distribution within the grain) can be sampled progressively from the grain boundary at the lowest temperature (T_1 – dark blue) to the grain core at the highest temperature (T_9 – red)

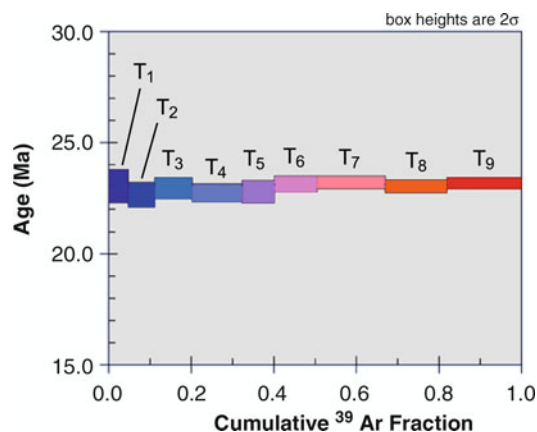


Fig. 3 Apparent age spectrum for a hypothetical grain with a uniform distribution of ^{40}Ar and $^{39}\text{Ar}_K$ throughout the grain. The horizontal length of each step corresponds to the fraction of $^{39}\text{Ar}_K$ from the total $^{39}\text{Ar}_K$ released and the vertical width corresponds to the apparent age and corresponding age uncertainty of that step (in this example, $\pm 2\sigma$). The color for each step corresponds to the region of the mineral grain in Fig. 2 from which the age of that step is derived. The weighted mean age from all of the steps yields an “integrated” age for the sample, which is equivalent to the age that would have been obtained if the sample was fused in a single step. If a significant fraction of the age spectrum (typically $>50\%$) is composed of steps having identical ages within error, then the weighted mean age of those steps is said to define a plateau age

Ar–Ar Data Interpretation

Because argon is a noble gas, its mobility within crystals is strongly dependent on temperature. Thus, the interpretation of Ar–Ar age spectra is based primarily on solid-state (volume) diffusion theory.

Plateau Ages

There is no convention that is widely accepted by the geochronology community as a standard definition of a plateau in an Ar–Ar age spectrum. Thus, the definition of a plateau should be explicitly stated where ambiguity may result. Common elements in any definition of a plateau generally include a series of contiguous steps which overlap within error and which comprise a significant fraction of the $^{39}\text{Ar}_K$ released from the sample. For example, the Fleck et al. (1977) definition states that a plateau is defined by three or more contiguous steps comprising at least 50 % of the $^{39}\text{Ar}_K$ released which overlap at the 2σ level. The plateau age is calculated as the weighted mean of the ages of all steps included in the plateau, with the inverse of the variance of the age of each step used as the weights. Examples of plateau age spectra are shown in Figs. 3–5.

The existence of a plateau is, in general, interpreted to indicate a uniform distribution of $^{40}\text{Ar}^*$ within that region of the mineral grain(s) sampled by those steps, and thus, a plateau age is often considered to be geologically meaningful. Understanding the geological context of the dated sample is critical in accurately interpreting a plateau age, however, because of argon’s ability to diffuse under elevated temperature conditions. For example, if the dated sample comes from a rapidly cooled igneous dyke which has undergone no metamorphism since intrusion, the plateau age may represent the actual formation age of the dyke. If the dated sample comes from a metamorphosed rock, however, the plateau age may represent the age of metamorphism rather than the protolith age, if the rock has been reheated to a temperature high enough for any accumulated argon to diffuse out of the mineral at the time of metamorphism, effectively “resetting” the Ar–Ar age of the mineral.

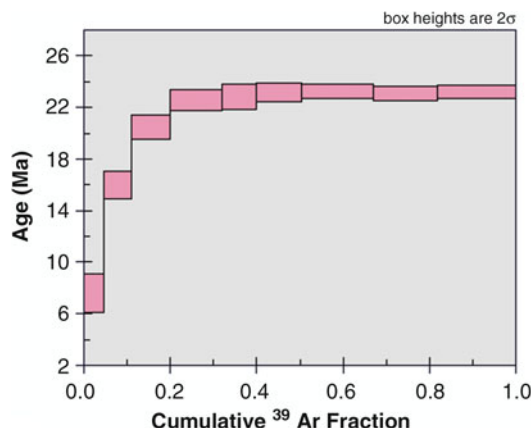


Fig. 4 Ar–Ar age spectrum exhibiting an argon-loss profile as defined by steps 1–3. Note that steps 4–9 still define a plateau with an age of ~23.6 Ma

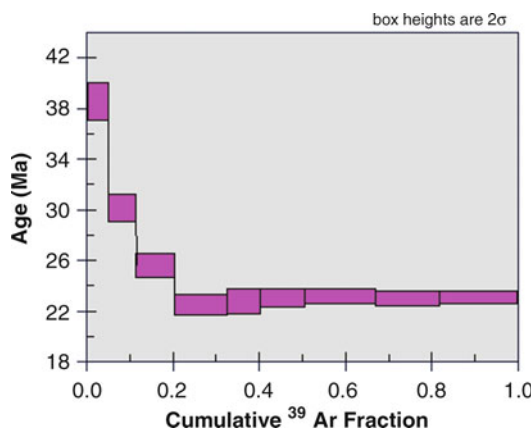


Fig. 5 Ar–Ar age spectrum exhibiting an excess-argon profile as defined by steps 1–3. Note that steps 4–9 still define a plateau with an age of ~23.6 Ma

An added complication in interpreting plateau ages arises in the step-heating of hydrous minerals such as amphiboles and micas. Gaber et al. (1988), Lee et al. (1991), Sletten and Onstott (1998), and Lo et al. (2000) found that during an Ar–Ar experiment, hydrous minerals may not remain stable at elevated temperatures due to oxidation and dehydroxylation of the crystal structure while being step-heated in vacuo. This structural decomposition of the crystal can lead to the formation of numerous extended defects throughout the grains and result in the homogenization of argon gradients which could lead to the generation of an apparent plateau (i.e., a pseudo-plateau) which has no geological significance. Thus, the plateau ages from such samples should be interpreted with caution.

Ar Loss

There are three main scenarios in which an age spectrum showing apparent Ar loss can be generated. The first is due to reheating. If a mineral has experienced a moderate–high T geological event, such as proximity to an igneous intrusion, contact metamorphism, hot fluid flow, etc., argon can diffuse out of the mineral. If argon diffusion is not sustained for protracted periods of time, it is possible that the mineral may experience only partial argon loss, such that argon is lost from a limited region of the grain nearest the grain boundary and the original argon is retained in the grain core. In this case, an apparent age spectrum may look like that in Fig. 4. A second scenario involves slow regional

cooling. If a mineral is subject to slow cooling resulting from regional-scale metamorphism or exhumation, partial argon loss can occur over long periods of time if the rate of cooling is not rapid enough to retard Ar diffusion. This will also yield an age spectrum similar to Fig. 4. Finally, a third scenario involves impurities (e.g., inclusions) in the analyzed crystals, which often degas in the lower T steps and can cause an apparent Ar-loss profile. Fortunately, it is often possible to determine if impurities are the cause by examining other argon isotopes (see section “Ca/K and Cl/K Spectra” below). Therefore, knowledge of the sample and its local geological context is important in interpreting such age spectra.

Excess ^{40}Ar

Thermal activation can also result in the diffusion of ^{40}Ar from the external environment into mineral grains, if the chemical potential of argon (often referred to as the argon partial pressure) is much greater outside the crystal than inside. Because this ^{40}Ar is not associated with the in situ decay of ^{40}K (i.e., radiogenic $^{40}\text{Ar}^*$), it is commonly referred to as excess Ar ($^{40}\text{Ar}_\text{E}$). There are many possible sources of excess Ar. One source is the host rock itself; if there are K-bearing minerals, local thermal reheating can release some of the $^{40}\text{Ar}^*$ to the surroundings, where it then becomes $^{40}\text{Ar}_\text{E}$. Another common source is hot Ar-rich fluids which may carry $^{40}\text{Ar}_\text{E}$ from the lower crust or distal regions. Incorporation of $^{40}\text{Ar}_\text{E}$ from the external environment means that age spectra tend to have anomalously old ages in the lower T steps (Fig. 5).

Sometimes, anomalously old ages are reflected in the highest T steps. Although the reasons for this will vary from sample to sample, one potential source is $^{40}\text{Ar}_\text{E}$ released from contaminant phases (e.g., pyroxene). Such phases may only release excess argon at high T or the phases may occur as internal inclusions which can only degas when the host mineral itself decomposes at high T . An example of an age spectrum displaying excess argon in the low and high T steps is shown in Fig. 6. An excellent review of the role of excess Ar in Ar–Ar dating may be found by Kelley (2002).

^{39}Ar Recoil

When a fast neutron interacts with a ^{39}K nucleus to form ^{39}Ar during neutron irradiation, there is a recoil energy also associated with this process. Turner and Cadogan (1974) calculated that the average recoil distance which an ^{39}Ar atom can move from the original position of the ^{39}K atom is $\sim 0.08\ \mu\text{m}$, which has been subsequently confirmed by direct experiment (Villa 1997). Although the ^{39}Ar recoil distance is very short compared to the length scale of most mineral grains (and therefore,

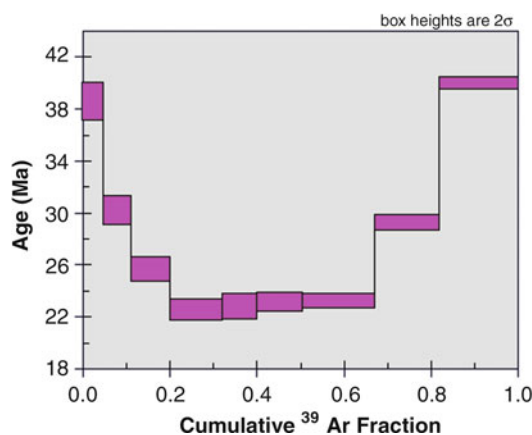


Fig. 6 Ar–Ar age spectrum exhibiting an excess-argon profile in the low and high T steps. This is sometimes referred to as a “saddle-shaped” age spectrum

will have a negligible effect in such cases), it can have a significant effect for very fine-grained materials (e.g., 1 μm) or samples with μm -scale domains, where the length scale of argon diffusion is of the same order of magnitude. In particular, it has been shown that significant ^{39}Ar loss can occur in minerals such as clays since it can be recoiled entirely out of the crystal structure (e.g., Halliday 1978). This has led to the development of encapsulation techniques when performing ^{40}Ar – ^{39}Ar dating on such fine-grained minerals, in which the sample is placed in a vacuum-evacuated, sealed capsule before irradiation in order to capture the ejected ^{39}Ar , which can then be measured subsequently in the mass spectrometer by breaking the capsule in vacuo and then reintegrating the measured ^{39}Ar trapped in the capsule into the step-heating results (e.g., Dong et al. 1995, 1997).

Alternatively, the recoiled ^{39}Ar may not be lost to the surrounding “void” but may become tightly imbedded in an adjacent K-poor phase. This is illustrated in Fig. 7.

For example, Huneke and Smith (1974) and Lo and Onstott (1989) observed this phenomenon occurring between a K-rich phase and olivine and biotite and chlorite, respectively. In such cases, the resultant age spectrum can display anomalously high ages in the low T steps (reflecting the loss of ^{39}Ar recoiled near the grain boundary) monotonically decreasing to anomalously low ages in the high T steps as the ^{39}Ar is degassed from the K-poor phases. Such an age spectrum is shown in Fig. 8.

For this reason, Ar–Ar studies involving fine-grained samples must interpret the results with care. In such specific situations, it may also be worthwhile to consider using conventional K–Ar dating, which avoids such difficulties.

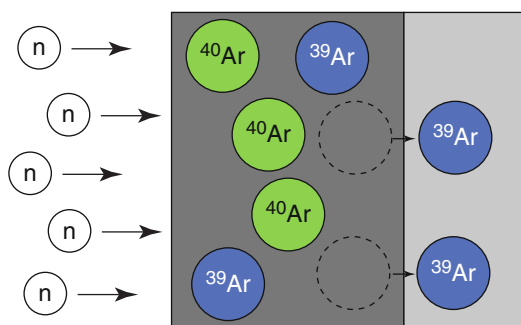


Fig. 7 ^{39}Ar recoil. Recoil energy from the fast-neutron conversion of ^{39}K can either eject ^{39}Ar atoms or reimplant them in adjacent phases, where they can be liberated at high temperature during a step-heating experiment

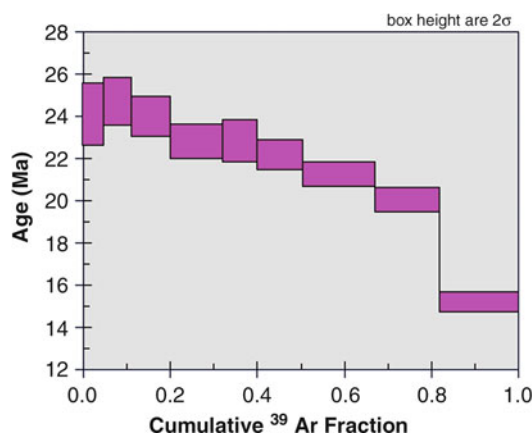


Fig. 8 Ar–Ar age spectrum exhibiting the effects of ^{39}Ar recoil artifacts. Anomalously high ages are seen in the first few steps which gradually decline to anomalously low ages in the final few steps

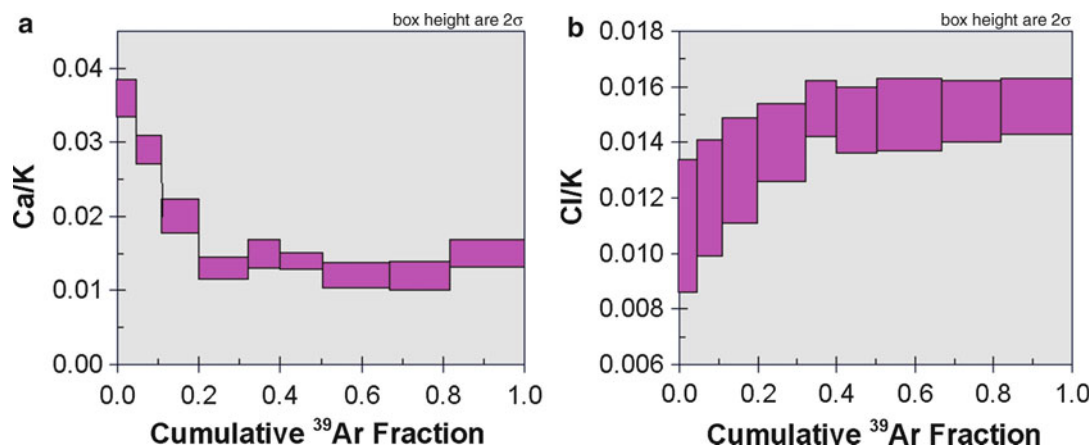


Fig. 9 (a) Ca/K spectrum showing elevated Ca/K ratios in the first three steps in comparison to the remaining steps. (b) Cl/K spectrum showing lower Ca/K ratios in the first three steps in comparison to the remaining steps. These spectra correspond to the same sample analyzed in Fig. 4. Such spectra can be useful in interpreting degassing patterns in Ar–Ar step-heating experiments

Ca/K and Cl/K Spectra

One useful aspect about the ^{40}Ar – ^{39}Ar technique is that it has the ability to yield significant information about the chemical composition of the samples that are being dated. The foundation of the ^{40}Ar – ^{39}Ar technique (through the $^{39}\text{K}(\text{n},\text{p})^{39}\text{Ar}$ reaction) already provides chemical information on the K content in the sample. As noted in the section on Data Corrections, however, there are also other neutron-induced interferences, leading to the production of ^{37}Ar from ^{40}Ca and ^{38}Ar from ^{37}Cl . Thus, an ^{37}Ar – ^{39}Ar ratio is directly related to a Ca/K ratio and an ^{38}Ar – ^{39}Ar ratio is directly related to a Cl/K ratio. Examples of Ca/K and Cl/K spectra are shown in Fig. 9.

These argon isotope ratios can provide useful information on the degassing of phases during a step-heating run. For example, consider Figs. 4 and 9. These spectra were all derived from the same sample, and a comparison of the first three steps in all of the spectra shows that the apparent argon-loss profile in Fig. 4 actually corresponds to argon released from a high Ca/K, low Cl/K reservoir, in contrast to a reservoir which has a uniform Ca/K and Cl/K over the steps corresponding to the plateau. This strongly suggests that the first three steps showing apparent argon-loss profile do not necessarily reflect a geologically meaningful event, but rather likely reflect argon released from a small amount of a contaminating phase, such as plagioclase or epidote. Note that this also does not necessarily affect the validity of the plateau age, but rather helps to discern the geological significance of various portions of an apparent age spectrum. A very illustrative study demonstrating the use of Ca/K spectra coupled with electron microprobe analyses to interpret a complex age spectrum is by Hanes et al. (1985).

Isochron Diagrams

The total amount of ^{40}Ar measured by a mass spectrometer during the analysis of an unknown for both K–Ar and Ar–Ar dating is a function of two main sources of ^{40}Ar – radiogenic ^{40}Ar from the in situ decay of ^{40}K in the sample ($^{40}\text{Ar}^*$) and any initial ^{40}Ar from the atmosphere ($^{40}\text{Ar}_i$). In other words,

$$^{40}\text{Ar}_{\text{total}} = ^{40}\text{Ar}_i + ^{40}\text{Ar}^* \quad (11)$$

This is analogous to many other geochronological systems, e.g., initial Sr in Rb–Sr and initial Pb in Pb–Pb. By substituting the K–Ar age equation of Eq. (1) into Eq. (11), we find

$$^{40}\text{Ar}_{\text{total}} = ^{40}\text{Ar}_i + \left(\frac{\lambda_e}{\lambda}\right)^{40}\text{K}(e^{\lambda t} - 1) \quad (12)$$

The difficulty in using Eq. (12) is that it is impossible to know exactly how much $^{40}\text{Ar}_i$ is in the sample, so to get around this, we divide Eq. (12) by stable, non-radiogenic, naturally occurring Ar isotope (^{36}Ar) to get

$$\left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{\text{total}} = \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_i + \left(\frac{\lambda_e}{\lambda}\right)(e^{\lambda t} - 1) \cdot \frac{^{40}\text{K}}{^{36}\text{Ar}} \quad (13)$$

In a plot of ($^{40}\text{Ar}/^{36}\text{Ar}$) versus ($^{40}\text{K}/^{36}\text{Ar}$), Eq. (13) has the form of a straight line $y = mx + b$. Note that the slope $m = (\lambda_e/\lambda)(e^{\lambda t} - 1)$ can therefore be used to determine the age t , and the y -intercept $b = (^{40}\text{Ar}/^{36}\text{Ar})_i$ is often the atmospheric ratio $(^{40}\text{Ar}/^{36}\text{Ar})_a = 295.5$.

In K–Ar dating, several minerals which have varying amounts of K (e.g., amphibole, biotite, and K-feldspar) from a rock sample are usually analyzed and the results are plotted on such a diagram. If the data form a straight line, this is termed a *mineral isochron* and the slope can therefore be used to calculate the age of the sample. An analogous procedure can be used to analyze whole-rock samples across a region, in which case a resultant line would be termed a *whole-rock isochron*. The goodness-of-fit of such lines is usually indicated by the mean square of the weighted deviates (MSWD) (McIntyre et al. 1966; York 1969).

In Ar–Ar dating, we substitute Eq. (9) into Eq. (11) to get

$$^{40}\text{Ar}_{\text{total}} = ^{40}\text{Ar}_i + \frac{(e^{\lambda t} - 1)}{J} \cdot ^{39}\text{Ar}_{\text{K}} \quad (14)$$

and dividing again by a stable, non-radiogenic, naturally occurring Ar isotope (^{36}Ar), we find

$$\left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_{\text{total}} = \left(\frac{^{40}\text{Ar}}{^{36}\text{Ar}}\right)_i + \frac{(e^{\lambda t} - 1)}{J} \cdot \frac{^{39}\text{Ar}_{\text{K}}}{^{36}\text{Ar}} \quad (15)$$

This is analogous to the K–Ar isochron equation [Eq. (13)], so in a plot of ($^{39}\text{Ar}/^{36}\text{Ar}$) versus ($^{40}\text{Ar}/^{36}\text{Ar}$), Eq. (15) has the form of a straight line $y = mx + b$. Note that the slope $m = (e^{\lambda t} - 1)/J$ can therefore be used to determine the age t , and the y -intercept $b = (^{40}\text{Ar}-^{36}\text{Ar})_i$ is often the atmospheric ratio $(^{40}\text{Ar}-^{36}\text{Ar})_a = 295.5$. An example of such an isochron diagram is shown in Fig. 10.

One feature of such isochron diagrams in Ar–Ar dating is that there is a strong correlation of uncertainties between the abscissa ($^{39}\text{Ar}-^{36}\text{Ar}$) and ordinate ($^{40}\text{Ar}-^{36}\text{Ar}$), shown by the rotated error ellipses which lie subparallel to the line in Fig. 10. This is a result of the common denominator (^{36}Ar) in each; because ^{36}Ar is such a small peak to measure in relation to ^{40}Ar , the relative uncertainty associated with measuring ^{36}Ar is much larger in relative terms and so this error correlation is significant.

To reduce this large correlation of errors, the inverse isochron (also known as isotope correlation) diagram places the largest measured peak (^{40}Ar) in the denominator.

Dividing Eq. (14) by $^{40}\text{Ar}_{\text{total}}$

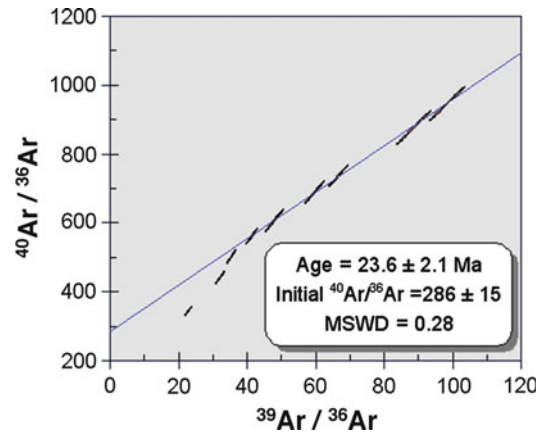


Fig. 10 Ar–Ar isochron diagram using the data obtained from the sample shown in Fig. 4. Note that the first three temperature steps do not lie on a line corresponding to the steps defining the plateau. A best-fit line through these steps yields a slope corresponding to an Ar–Ar isochron age of 23.6 Ma, which is identical to the plateau age

$$1 = \frac{{}^{40}\text{Ar}_i}{{}^{40}\text{Ar}_{\text{total}}} + \frac{(e^{\lambda t} - 1)}{J} \left(\frac{{}^{39}\text{Ar}}{{}^{40}\text{Ar}} \right)_{\text{total}} \quad (16)$$

If ${}^{40}\text{Ar}_i = {}^{36}\text{Ar}_i \cdot v$, where v is the initial $({}^{40}\text{Ar}/{}^{36}\text{Ar})_i$ ratio, then

$$1 = \frac{{}^{36}\text{Ar}_i \cdot v}{{}^{40}\text{Ar}_{\text{total}}} + \frac{(e^{\lambda t} - 1)}{J} \left(\frac{{}^{39}\text{Ar}}{{}^{40}\text{Ar}} \right)_{\text{total}} \quad (17)$$

and dividing by v :

$$\left(\frac{{}^{36}\text{Ar}}{{}^{40}\text{Ar}} \right)_{\text{total}} = \frac{1}{v} - \frac{(e^{\lambda t} - 1)}{Jv} \left(\frac{{}^{39}\text{Ar}}{{}^{40}\text{Ar}} \right)_{\text{total}} \quad (18)$$

In a plot of $({}^{39}\text{Ar}/{}^{40}\text{Ar})$ versus $({}^{36}\text{Ar}/{}^{40}\text{Ar})$, Eq. (18) has the form of a straight line $y = mx + b$. Note that in this case, y -intercept $b = 1/v$ is often the inverse of the atmospheric ratio $({}^{40}\text{Ar}-{}^{36}\text{Ar})_a = 1/295.5 = 3.384 \times 10^{-3}$, and the x -intercept (when the ${}^{36}\text{Ar}-{}^{40}\text{Ar}$ equals zero) is simply ${}^{39}\text{Ar}/{}^{40}\text{Ar}^* = J/(e^{\lambda t} - 1)$ from Eq. (8) and therefore yields an *intercept age* t . An example of an inverse isochron diagram is shown in Fig. 11.

The data which form a line on an isotope correlation diagram can be interpreted to reflect mixing between two Ar reservoirs (or components) in the sample. More complex mixing patterns between different argon reservoirs within a crystal may also be discerned using such diagrams (e.g., Phillips and Onstott 1988). Sometimes, Ar–Ar isochron diagrams may be somewhat misleading because nonlinear data may *appear* to have a good linear correlation because of the strong correlation of errors; however, Dalrymple et al. (1988) have shown that there is no difference between isochron versus inverse isochron plots as long as rigorous mathematics for the least squares fitting of lines with correlated errors is used.

Probability Distribution Diagrams

Probability distribution diagrams (Fig. 12) are generally used to plot the cumulative results of a group of single-grain total fusion analyses. Analogous to histograms, the diagrams plot the age on

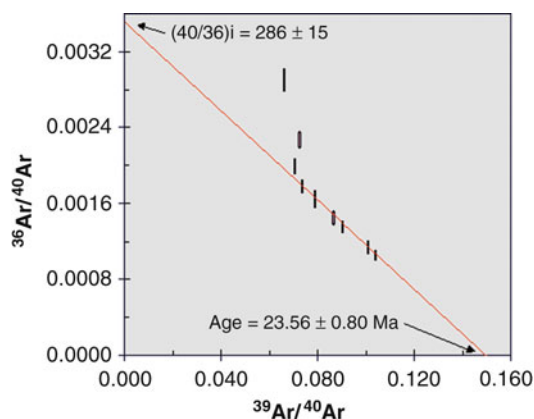


Fig. 11 Ar–Ar inverse isochron diagram using the data obtained from the sample shown in Fig. 4. Note that the first three temperature steps do not lie on a line corresponding to the steps defining the plateau. A best-fit line through these steps yields an intercept age of 23.6 Ma, which is identical to the plateau age in Fig. 4 and the isochron age in Fig. 10

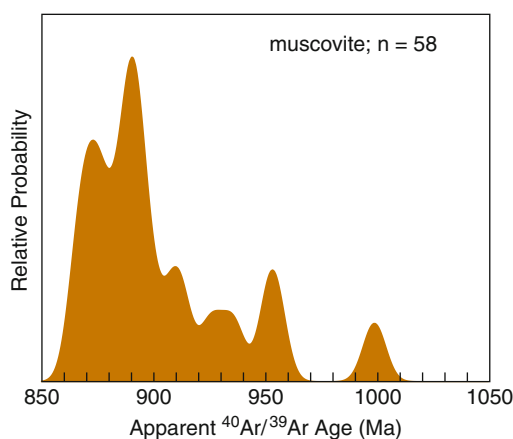


Fig. 12 Probability distribution diagram of the Ar–Ar ages from 58 single crystals of detrital muscovite derived from a sandstone. The higher the peak, the greater the number of grains of that age. In this example, the muscovite grains appear to be derived from at least three different sources or regions – a dominant source with an age of 880–890 Ma, another source with an age of ~950 Ma, and a third (minor) source with an age of ~1,000 Ma

the x-axis versus the relative probability (i.e., the sum of the normal distributions of the individual analyses of single-grain total fusion ages based on their experimental uncertainties; Deino and Potts 1992). They are particularly useful in detrital provenance studies where source regions of different ages can be distinguished.

Argon Terminology

There are several possible sources of argon in rocks. The following glossary describes these various sources:

Artificially induced Ar – argon (typically ^{36}Ar , ^{37}Ar , ^{38}Ar , ^{39}Ar , or ^{40}Ar) produced in a mineral during fast-neutron irradiation in a nuclear reactor, due to neutron interactions with Cl, Ca, and K.

Atmospheric Ar – argon from the atmosphere, may be either $^{36}\text{Ar}_a$, $^{38}\text{Ar}_a$, or $^{40}\text{Ar}_a$. The present-day $^{40}\text{Ar}_a/^{36}\text{Ar}_a$ is 295.5.

Cosmogenic Ar – any Ar isotope (typically ^{36}Ar , ^{37}Ar , ^{38}Ar , ^{39}Ar , or ^{40}Ar) produced from cosmic ray interactions with various elements (including Ca, Ti, Fe) in a mineral, mainly through spallation reactions, but also through neutron capture, normally only a concern when dealing with extraterrestrial samples.

Excess Ar – any Ar (typically ^{40}Ar) which is incorporated into minerals by processes other than the in situ radioactive decay of ^{40}K in the crystal, includes inherited Ar but may also include Ar derived from physical contamination by other minerals or Ar introduced into a crystal from other sources after its formation, e.g., by metamorphic fluids.

Inherited Ar – argon (typically ^{40}Ar) incorporated into the crystal lattice of a mineral at the time of its formation which is NOT associated with the radiogenic $^{40}\text{Ar}^*$ produced from the in situ decay of ^{40}K in the crystal (see *excess Ar*). This is one form of excess Ar.

Radiogenic Ar – $^{40}\text{Ar}^*$ formed from the in situ decay of ^{40}K in a mineral.

Trapped Ar – argon that is trapped within a rock or mineral at the time of its formation or during a subsequent event, can exist in the crystal lattice (= *inherited Ar*) or as fluid inclusions (which would typically be expected to contain Ar of atmospheric composition for terrestrial samples).

Applications

K–Ar

At present, there are two main uses of the conventional K–Ar method. First, it can be used to calibrate fundamental physical parameters such as the K decay constant, since it is a method grounded on first principles, i.e., the method is completely independent of other geochronological methods. Second, it is well-suited for dating potassium-bearing fine-grained materials (such as clays or glauconites) where ^{39}Ar recoil would be problematic.

In general, however, the method of choice for dating most K-bearing materials in a variety of geological studies is the Ar–Ar method.

Ar–Ar

The presence and abundance of K-bearing minerals in a variety of rocks, coupled with the strong temperature dependence of argon diffusion in minerals, have led to the widespread application of Ar–Ar dating in a variety of geological applications. There are a plethora of studies in each of the general areas below which are far too numerous to list; some illustrative references are included, and more can also be found in more specific entries cross-referenced in this work.

In general, Ar–Ar dating has been applied most often in the following areas of study which are described briefly below.

Refinement of the Geological Time Scale and Time-Scale Boundaries

Ar–Ar dating and U–Pb dating are currently the most commonly used techniques in establishing the timing of geological events that are used to mark the various temporal boundaries in the geological time scale. The accuracy and precision of both of these methods remain unmatched by any other geochronological technique. Ar–Ar dating has been used to refine the age of many boundaries such as the Cretaceous–Paleogene boundary by dating the age of the Chicxulub crater off the coast of Mexico (e.g., Renne et al. 2013) or the Permian–Triassic boundary by dating large-scale flood basalts (e.g., Reichow et al. 2009).

Hominid Evolution

The high precision of the Ar–Ar technique makes it an excellent method in which to date fossil evidence of the earliest origins of the human species. By precisely dating minerals (such as sanidines) from volcanic ash beds which lie above and below fossilized remains, Ar–Ar dating has proven to be extremely useful in understanding the evolution of hominids. Examples of Ar–Ar studies include the dating of hominid evolution in western Africa (e.g., Leakey et al. 1995, 1998), the earliest hominids in Java (Swisher et al. 1994), and early hominids in Georgia (Gabunia et al. 2000), which appear to shift the date of hominid dispersal out of Africa at least half a million years earlier than previously thought. Antón and Swisher (2004) provide a general review of hominid evolution out of Africa, and an overview of the method applied to paleoanthropology and archeology is provided by Deino et al. (1998).

Thermochronology

Because Ar is a noble gas, it is particularly sensitive to temperature. If ambient temperatures are high enough, Ar will preferentially leave the mineral structure via diffusive transfer and escape to the surroundings. Thus, rocks which have been reheated after crystallization (e.g., due to metamorphism) may partially or completely lose Ar from their minerals, depending on the diffusion characteristics of the mineral, the temperature, and the time involved. The temperature dependence of Ar–Ar ages has opened up an entire field of geochronology known as thermochronology where the thermal evolution of rocks and regions can be studied using multiple geochronological techniques; of these, Ar–Ar technique is one of the most versatile.

As mentioned in the section on Modes of Analysis, the interpretation of argon data is fundamentally based on solid-state diffusion theory. There is now a considerable body of knowledge associated with the application of diffusion theory in geochronology, starting with the landmark paper by Dodson (1973), who developed the mathematics defining the concept of *closure temperature* (T_c). This key concept, which is defined as the temperature of a cooling system at the time defined by the age of a mineral, has led to the development of field thermochronology, in which the thermal (i.e., temperature T , time t) histories of rocks and regions can be elucidated with geochronological techniques. Because argon diffuses at different rates in minerals (due to difference in chemical composition and the structure of the crystal lattice), different K-bearing minerals span a different range of Ar closure temperatures. Argon diffusion experiments have determined that, in general, for K-bearing minerals having the same length scale of diffusion (i.e., grain size) and cooling rate, argon closure temperatures increase in the following order: T_c (K-feldspar) < T_c (biotite) < T_c (muscovite) < T_c (hornblende). As a result, studying rocks having these minerals means that an Ar–Ar dating study could elucidate thermal histories over a temperature range of potentially 150–600 °C; this temperature range covers a significant portion of the thermal history of many rocks, making Ar–Ar thermochronology a very powerful tool in the study of the evolution of geological terranes. Complicated numerical models attempting to deconvolute thermal histories from the step-heating of single crystals of K-feldspar have been developed (e.g., the multidiffusion domain (MDD) model of Lovera et al. 1989 and subsequent papers thereafter), but these remain controversial because of a lack of correspondence to actual physical features which are observed in the analyzed minerals, both in nature and during argon step-heating experiments (see Parsons et al. 1999, 2010). The entry on Thermochronology provides more details on the fundamental principles of this field.

Many thermochronological Ar–Ar studies have been conducted throughout the world, spanning most of the Earth's history. One of the earliest Ar–Ar thermochronological studies was by Berger and York (1981), who analyzed hornblende, biotite, plagioclase, and K-feldspar to determine the

cooling history of the Haliburton Highlands in the Grenville Province, Ontario. An overview of many of these studies and a more detailed analysis of thermochronological principles can be found in McDougall and Harrison (1999).

Structural Geology

Ar–Ar dating has found widespread application in solving structural geology problems because it can date K-bearing phases (especially micas) that form during deformational events. Moreover, the development of the laser microprobe in Ar–Ar dating (see “► [Single Crystal Laser Fusion](#)”) enables mineral grains to be dated in situ and, thus, potentially allows multiple deformation events to be dated in a single rock. Many recent studies have also highlighted the importance of considering defect structures associated with deformation in controlling Ar mobility and therefore in interpreting Ar–Ar ages; the study of white micas by Kramar et al. (2001) highlights the utility of the ^{40}Ar – ^{39}Ar laser microprobe in this regard.

Tectonics

The ability to document a significant portion of the low–mid-temperature history of geological terranes has made Ar–Ar dating the method of choice in many tectonic studies. In general, thermochronology is used to elucidate regional thermal T – t histories by dating a variety of K-bearing minerals that record different parts of the geological evolution of a terrane. Many Ar–Ar applications in tectonics have been published. A novel application of Ar–Ar thermochronology was presented by Camacho et al. (2005), who used a variety of Ar–Ar techniques in combination with diffusion theory to determine the duration of a complete orogenic cycle (subduction and exhumation) in the Bergen Arcs of Norway.

Economic Geology

Ar–Ar dating is well suited for the timing of mineralization in ore deposits because K-bearing minerals are commonly associated either with the ore or with ore-forming processes. Minerals such as biotite, K-feldspar, muscovite, and alunite are commonly dated in such studies. Ar–Ar dating has been applied in the study of a variety of ore deposits including porphyry Cu–Mo (e.g., Quang et al. 2003), epithermal Au (e.g., Bissig et al. 2002), vein Au (e.g., Kontak et al. 1998; Mark et al. 2010), Mississippi Valley-type Pb (e.g., Sherlock et al. 2004), unconformity-type U (e.g., Polito et al. 2004), and diamondiferous kimberlitic (e.g., Phillips et al. 1999) deposits.

Detrital Provenance

Ar–Ar dating of single crystals of K-bearing minerals has provided useful insights into the provenance of sediments derived from adjacent source regions. Analogous to the U–Pb dating of single crystals of zircon, the dating of grains of detrital biotite and muscovite can be equally useful if the thermal history of the rocks has not been substantially disturbed. A recent overview of the use of Ar–Ar dating in detrital provenance studies is given in Hodges et al. (2005).

Paleomagnetism and the Geomagnetic Polarity Time Scale

Ar–Ar dating has been particularly useful in dating paleomagnetic poles for plate reconstructions as well as in refining the geomagnetic polarity time scale. An excellent summary is given in York (1984) with subsequent developments outlined in Spell and McDougall (1992).

Sedimentary Basin Evolution

Sedimentary basins have been the subject of intense study because of the opportunity to study a wealth of crustal processes as well as a rich source of ore and hydrocarbon deposits. Ar–Ar dating is generally considered to record higher-temperature processes in such basins and is also used in the study of the provenance of sediments. A recent overview of the use of Ar–Ar and other thermochronometers in understanding the thermal histories of sedimentary basins is given in Armstrong (2005).

Cosmochronology

One of the earliest applications of ^{40}Ar – ^{39}Ar dating was in the study of meteorites as well as lunar samples brought back from the US Apollo missions. In particular, there is a vast body of literature on the ^{40}Ar – ^{39}Ar dating of whole-rock basalts and related rocks which led not only to an increased understanding of the genesis of the moon and solar system but also to many refinements in the development of the technique. Many of these results are summarized in McDougall and Harrison (1999).

Advantages and Limitations

With a ^{40}K half-life of 1,250 Ma, the K–Ar and Ar–Ar methods are well-suited for dating most geological materials from the Paleocene to the age of the Earth and solar system. Dating very young materials, e.g., < 1 Ma, can be particularly challenging with the Ar–Ar method due to very short irradiation times and larger uncertainties resulting from variations in the neutron flux and proportionally larger corrections from blanks, neutron interferences, and mass discrimination in the mass spectrometer. However, extremely young rocks dating from historical times (i.e., the eruption of Mt. Vesuvius in 79AD) have been successfully dated using the Ar–Ar method (Renne et al. 1997; Lanphere et al. 2007).

In addition, the K–Ar and Ar–Ar dating methods occupy a unique position among all geochronological methods because Ar is a noble gas. As K–Ar and Ar–Ar ages are therefore particularly dependent on the temperature of geological systems, this has both its advantages and disadvantages. In particular, one of the greatest strengths is the ability to record the geological history of a sample over a range of temperatures. However, in the absence of additional geological and petrological information, it may not be possible to know if a K–Ar or Ar–Ar age represents a crystallization, metamorphic, or cooling age.

K–Ar

At present, there are two main advantages of the conventional K–Ar method. First, it is a method grounded on first principles, i.e., the method is completely independent of other geochronological methods. This is essential where reevaluation of fundamental physical parameters such as the K decay constant may be important (see section “[Radioactive Decay Scheme](#)”). Second, it is well suited for dating potassium-bearing fine-grained materials (such as clays or glauconites) where ^{39}Ar recoil would be problematic.

A major disadvantage of the K–Ar method is the sensitivity of a K–Ar age to the thermal history of the rocks. While a K–Ar age may reflect the formation age or crystallization age of rocks, this age can be readily disturbed or even reset due to a variety of geological processes such as slow cooling, thermal reheating, or regional metamorphism. For example, in many early studies, it was noted that K–Ar dates did not agree with either (a) dates for other potassium-bearing minerals from the same

rock or (b) ages using other geochronological methods (e.g., Rb–Sr, U–Pb). Thus, one of the most serious challenges with the conventional K–Ar method is that, in isolation, it is impossible to tell whether a K–Ar date reflects the time of crystallization, time of a subsequent metamorphism, or some time in between. There are some other disadvantages with conventional K–Ar dating. In the K–Ar method, absolute quantities of potassium and argon are measured on separate aliquots of the sample in order to calculate the ^{40}Ar – ^{40}K ratio and, hence, the age of the sample; consequently, K–Ar ages tend to have much larger uncertainties than Ar–Ar ages. Moreover, if the sample is inhomogeneous, this practice can significantly reduce the accuracy of the final age. In addition, because the sample is completely fused to measure K and Ar, only a single date can be obtained per analysis. Finally, relatively large quantities (milligrams) of pure sample are required for a K–Ar analysis which means that there must be significant quantities of sample available to be analyzed, also increasing sample preparation requirements.

Fortunately, all of these disadvantages are effectively eliminated by using the ^{40}Ar – ^{39}Ar technique.

Ar–Ar

There are numerous advantages in using the ^{40}Ar – ^{39}Ar method. It is more convenient in terms of analysis because only isotopes of Ar need to be measured from a single aliquot of sample, unlike K–Ar dating in which different techniques are required to measure K and Ar, respectively. Problems with sample inhomogeneity and differing machine calibrations are eliminated because all of the measurements are performed on the same sample with the same equipment. Because only ratios are needed (i.e., $^{40}\text{Ar}/^{39}\text{Ar}$), Ar–Ar ages will inherently be more precise than K–Ar ages and can typically achieve routine analytical uncertainties less than $\pm 0.5\%$. The high sensitivity of today's noble gas mass spectrometers means that very little sample is required for analysis; single-grain dating is routine. A variety of techniques (furnace/laser step-heating, total fusion, laser spot-fusion) can be employed to suit the goals of the project. The method can yield significant information on the thermal history of the sample. Finally, other argon isotopes can be used to infer some information about the chemical composition (K, Ca, Cl) of the sample.

Ar–Ar dating does have some disadvantages. A nuclear reactor with a suitable fast-neutron fluence is required. This also means that irradiated samples are radioactive and must be appropriately stored; safe handling and sample preparation procedures must also be developed. Neutron irradiation results in the formation of artificial Ar isotopes from K, Ca, and Cl which must be corrected in calculating an Ar–Ar age, leading to more complicated data processing. The irradiation also results in ^{39}Ar recoil, which can negatively affect the ages of very fine-grained samples or samples with μm -scale domains. Finally, all of these factors also mean that the method is generally more time consuming and costly in comparison to K–Ar dating.

Summary

The Ar–Ar method has largely superseded conventional K–Ar dating because of its numerous advantages. The presence of K-bearing minerals in a variety of rocks has led to the widespread application of Ar–Ar dating to solve a variety of geological problems involving the geological time scale, hominid evolution, structural geology and tectonics, economic geology, detrital provenance, paleomagnetism, the evolution of sedimentary basins, and the origin of extraterrestrial materials. Moreover, the strong relationship between argon mobility and temperature makes the Ar–Ar method an ideal thermochronometer. To apply it successfully, however, knowledge of the microstructural,

mineralogical, petrological, and geological context of the dated samples must be known in order to obtain meaningful interpretations of the age data. With this information, the real power of the Ar–Ar method lies in its unique ability to solve diverse problems in the earth sciences and to elucidate a significant portion of the temperature–time histories of geological terranes.

Cross-References

- ▶ [Age of the Earth](#)
- ▶ [Alpine Terranes \(K-Ar / Ar-Ar\)](#)
- ▶ [Clays and Glauconites \(K-Ar / Ar-Ar\)](#)
- ▶ [Cretaceous-Tertiary Boundary](#)
- ▶ [Extraterrestrial Materials \(K-Ar / Ar-Ar\)](#)
- ▶ [Geochronology](#)
- ▶ [Geological Time Scale](#)
- ▶ [Hominid Evolution Timescale Chixculub](#)
- ▶ [Igneous Rocks \(K-Ar / Ar-Ar\)](#)
- ▶ [Kimberlites \(K-Ar / Ar-Ar\)](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Metamorphic Terranes \(K-Ar / Ar-Ar\)](#)
- ▶ [Minerals \(Ar-Ar\)](#)
- ▶ [Noble Gas Mass Spectrometer](#)
- ▶ [Paleomagnetic Poles \(K-Ar / Ar-Ar\)](#)
- ▶ [Provenance \(Thermochronology\)](#)
- ▶ [Single Crystal Laser Fusion](#)
- ▶ [Structural Fabrics \(K-Ar / Ar-Ar\)](#)
- ▶ [Tektites](#)
- ▶ [Thermochronology](#)
- ▶ [Volcanic Rocks \(K-Ar / Ar-Ar\)](#)

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Single-Crystal Laser Fusion

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Synonyms

Laser spot dating; Single-crystal step-heating; Single-crystal total fusion

Definition

An analytical technique in Ar–Ar ($^{40}\text{Ar}/^{39}\text{Ar}$) dating in which a laser is used to heat single crystals of minerals in order to extract argon isotopes for measurement in a mass spectrometer.

Introduction and Modes of Operation

Improvements in the sensitivity of argon mass spectrometers have enabled the measurement of argon isotopes released from the single crystals of K-bearing minerals. In order to release the argon from the crystal structure, in an environment with minimal contamination from the atmosphere and experimental conditions, lasers have been employed in combination with low-volume extraction lines and sample chambers. The earliest use of lasers in single-crystal Ar–Ar dating was by Megrue (1967), who employed a pulsed ruby laser to analyze meteorite samples. York et al. (1981) documented the first use of a continuous-wave laser in a thermochronological study of metamorphic rocks and showed that such lasers could be used to progressively step-heat a single crystal to obtain an apparent age spectrum, analogous to that obtained by heating a much larger aliquot of crystals in a furnace. Further information about the step-heating technique and the interpretation of Ar–Ar age spectra can be found in the section “K–Ar and Ar–Ar Dating.” Since then, the use of single-crystal laser dating techniques in Ar–Ar dating has become widespread. Figure 1 shows a typical laser dating system and Fig. 2 shows a close-up of the sample chamber containing mineral grains to be analyzed.

Single-crystal $^{40}\text{Ar}/^{39}\text{Ar}$ laser dating can be performed in three modes: (1) step-heating, (2) total fusion, and (3) spot dating.

Laser Step-Heating

In laser step-heating, a large-diameter, defocused laser beam is used to progressively heat single crystals in a series of steps of increasing power (i.e., temperature) until the crystal has completely melted and fused into a glass bead. At each step, the argon isotopes released by the heating are analyzed in a mass spectrometer to obtain an $^{40}\text{Ar}/^{39}\text{Ar}$ age for that step. A defocused beam is essential in order to uniformly heat the entire crystal in each step. The complete sequence of steps

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Fig. 1 $^{40}\text{Ar}/^{39}\text{Ar}$ laser system. The laser (in this case, a Lexel Ar-ion laser) sits horizontally on the bench. Mineral grains are placed inside the cylindrical steel sample chamber (see Fig. 2) on the *right-hand side* of the photograph on the stage of the binocular microscope. A CCD camera is aligned along the optical axis of the microscope and laser beam so that mineral grains can be viewed “live” on the television screen (at the *left*) as they are heated. The laser power is controlled by the rectangular console (foreground, *left*) and the sample chamber can be moved precisely in small increments in both the X and Y directions using the joystick controller (foreground, *center*)

(from low to high temperature) yields an $^{40}\text{Ar}/^{39}\text{Ar}$ apparent age spectrum. This technique can be

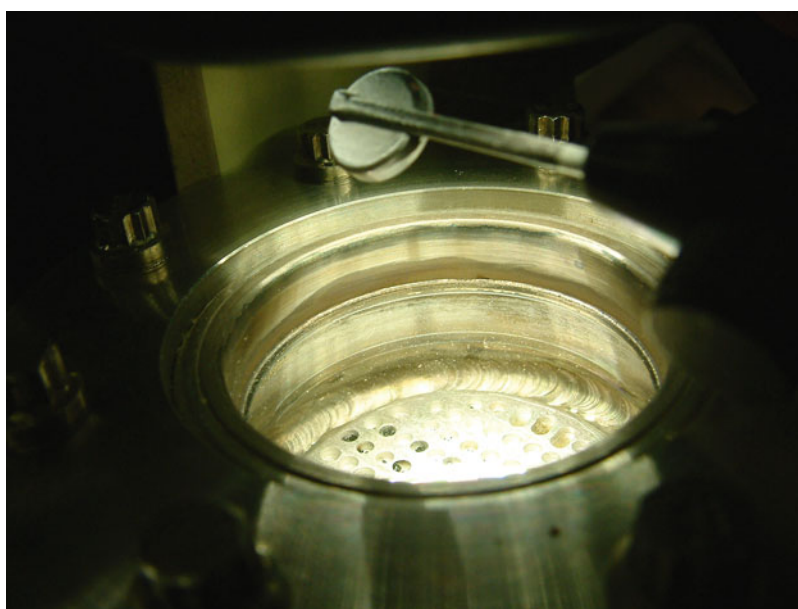


Fig. 2 Laser dating sample chamber. Single crystals of the samples to be analyzed are placed in small holes drilled into a metal (e.g., Al or Cu) planchet (*bottom, center*). The planchet is then placed inside a steel sample chamber with a viewport that is transparent to the laser beam radiation, and the chamber is evacuated under ultrahigh vacuum. In this system, the laser beam comes in horizontally from the *upper right* of the photo and is deflected downwards onto the mineral grains in the planchet by a circular mirror angled at 45° (*top, center*)

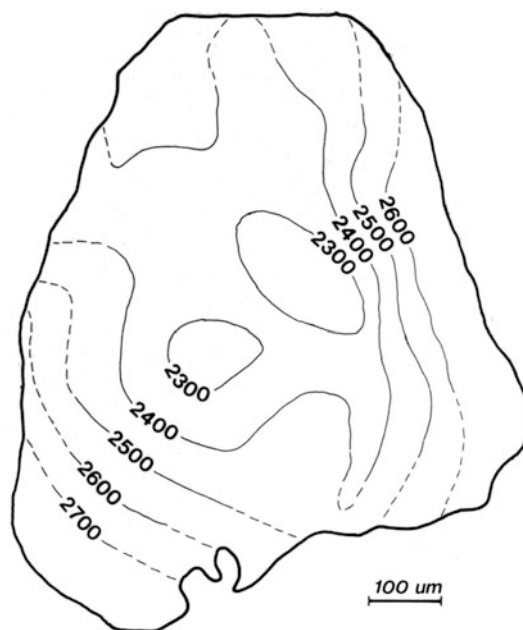


Fig. 3 Age contour or “chrontour” map of a single amphibole grain with an age gradient ranging from ~2,300 Ma in the grain core to ~2,700 Ma along the grain rim. Chrontours were constructed from 22 individual laser spot dates obtained within the grain (Modified after Lee et al. (1990))

used to elucidate potential age gradients within crystals from rocks which may have cooled slowly or been partially reset due to metamorphism or local reheating. One of the earliest geological applications is given by York et al. (1981). Lee et al. (1990) used both laser step-heating and laser spot dating (described below) to elucidate age profiles from rocks in a contact metamorphic zone. Laser step-heating is now one of the most common modes of single-grain laser dating. Typical types of lasers currently used for this mode of dating are continuous-wave lasers that emit in the infrared (IR) and visible wavelengths, such as CO₂ and Ar-ion lasers.

Laser Total Fusion

In single-crystal total fusions, a laser is used to completely fuse a single mineral crystal in one step using a focused or slightly defocused beam. The released argon isotopes are analyzed in a mass spectrometer to obtain an $^{40}\text{Ar}/^{39}\text{Ar}$ age for the crystal. This age is identical to the integrated age that would be obtained from an $^{40}\text{Ar}/^{39}\text{Ar}$ apparent age spectrum. Because this mode produces only a single age per crystal, it is most typically used in dating studies in which there may only be a limited amount of sample or in detrital or provenance studies of crystals which may have come from a variety of source rocks or regions which therefore reflect rocks of different ages. The data are commonly displayed in the form of a probability density diagram of total fusion age versus relative probability (i.e., frequency) (see K–Ar and Ar–Ar Dating). A thorough overview summarizing a variety of $^{40}\text{Ar}/^{39}\text{Ar}$ detrital studies is given by Hodges et al. (2005). Typical types of lasers currently used for this mode of dating are continuous-wave or pulsed lasers that emit in the infrared (IR), visible, and ultraviolet (UV) wavelengths, such as CO₂, Ar-ion, and Nd:YAG lasers.

Laser Spot Dating

In laser spot dating, a finely focused laser beam is used to ablate small volumes of sample *within* single crystals. The argon isotopes released by the ablation are analyzed to yield an age for that spot. Samples are usually prepared in the form of a single crystal with a flat surface perpendicular to

the laser beam (e.g., as a polished thick section) such that the laser can be used effectively as an age microprobe, in which laser spot traverses can be conducted from the core to the rim of a single crystal. Age contour (or “chrontour”) maps across an entire crystal can be constructed (Fig. 3) if a suitable number of sampling points can be obtained, e.g., Phillips and Onstott (1988), Lee et al. (1990), and Kramar et al. (2001). Typical laser beam diameters can produce spots as small as 5–10 μm in diameter, though typical applications employ larger (e.g., 20–50 μm) spots in order to reduce analytical uncertainties. This mode of dating is used to directly ascertain potential age gradients within crystals. A variant of this mode involves rastering the laser beam over a large area of the crystal (e.g., $100 \times 100 \mu\text{m}$) or drilling a line of spots in the form of a “trench” in order to obtain enough argon to measure in a single analysis with reasonable precision, e.g., Kelley and Wartho (2000). This variant is most commonly employed in Ar diffusion studies or in depth profiling. Typical types of lasers currently used for this mode of dating are pulsed lasers that emit in the IR and UV wavelengths, such as Nd:YAG, frequency-quadrupled Nd:YAG, and excimer lasers.

Advantages and Limitations

$^{40}\text{Ar}/^{39}\text{Ar}$ single-crystal laser dating has a number of advantages. Single-crystal analysis enables the unambiguous measurement of the distribution of Ar isotopes within a crystal, i.e., it eliminates the potential for the mixing of different Ar reservoirs from various sources which may exist in analyzing a mineral separate composed of tens or hundreds of mineral grains. In addition, the effects of contamination from other minerals or phases that may be present in larger aliquots of minerals can be reduced. Another advantage is that the amount of material that is required for analysis is significantly reduced, which may be particularly important in the analysis of trace or rare minerals. The reduced sample size also greatly simplifies and reduces the time required to prepare samples for analysis and also minimizes the volume of sample that must be artificially irradiated and safely stored.

This technique also has some limitations. The reduced sample size means that volumes of Ar derived from laser heating are proportionally smaller; this means that sufficiently old, K-rich, or large crystals should be dated to provide ages with acceptable precision. Alternatively, modified techniques such as rastering or trenching (discussed above) should be used. The smaller gas volumes generally mean that age uncertainties on single-crystal laser ages are somewhat larger than those derived from analyzing larger aliquots of sample. For laser step-heating, it is important that the laser radiation couples well with the mineral structure to ensure uniform heating of the crystal; for example, although Nd:YAG lasers have been successfully used to step-heat mafic minerals such as biotite and amphibole, they are known to have difficulty coupling with optically transparent minerals such as K-feldspar. Care must also be taken when performing laser spot dating analyses on single crystals which are inhomogeneous, e.g., those with exsolution lamellae or Ar reservoirs, as the resultant ages may reflect the ages of the different phases/reservoirs or a combined mixture of their ages.

Summary

Single-crystal laser dating techniques are now commonly employed in Ar–Ar dating studies. Depending on the type of application, either pulsed lasers or continuous-wave lasers may be used. Continuous-wave lasers are typically used for single-crystal step-heating and total fusions;

in this case, the laser beam radiation must couple well with the mineral structures to be heated (i.e., laser energy needs to be efficiently absorbed by the mineral), and CO₂ lasers are most commonly used in current applications because the wavelength of the radiation appears to couple efficiently with all oxygen-bearing compounds. Pulsed lasers are typically used for laser spot dating; UV wavelengths are commonly employed because of the improved efficiency in ablating a large variety of silicate minerals. Numerous advantages of single-crystal dating have led to its widespread application in a variety of Ar–Ar dating studies.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Geochronology](#)
- ▶ [Igneous Rocks \(K-Ar\)](#)
- ▶ [Noble Gas Mass Spectrometer](#)
- ▶ [Kimberlites \(K-Ar/Ar-Ar\)](#)
- ▶ [Minerals \(Ar-Ar\)](#)
- ▶ [Metamorphic Terranes \(K-Ar/Ar-Ar\)](#)
- ▶ [Provenance \(Thermochronology\)](#)
- ▶ [Thermochronology](#)
- ▶ [Volcanic Rocks \(K-Ar/Ar-Ar\)](#)

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Alpine Terranes (K-Ar/Ar-Ar)

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Synonyms

Tertiary metamorphic terranes; Young metamorphic terranes

Definition

Alpine terranes in the strictest sense can be defined geographically as terranes belonging to the region in south–central Europe from the Maritime Alps and Ligurian Alps along the Mediterranean coast between Genova and Marseille in the west and the Vienna basin in the east where the Tauern window ends in the northern belt and the Julian Alps of Slovenia in the southern belt.

In a geological sense, much of southern Europe from the Betics in southern Spain and the Rif in northern Morocco to the Hellenides in Greece much of southern Europe forms part of the Alpine orogeny. In fact, when viewed as resulting from the collision of the Arabian–African continent in the south and Eurasia in the north, the Alpine orogeny can be traced much further to the southeast to include Turkey and metamorphic complexes along the Persian Gulf to end in Oman in the far southeast (Fig. 1).

The term Alpine terranes is sometimes used to include young Tertiary mountain belts worldwide.

When approached from the perspective of metamorphic processes, the Alpine terranes include the crystalline cores of orogens formed by metamorphic processes since the Cretaceous. Alpine terranes thus form a subset of the metamorphic terranes.

Introduction

For the purpose of the present summary, it is useful to propose a mixed definition based mainly on timing of metamorphic processes but including geographical considerations. Alpine metamorphic terranes contain the evidence for processes that deformed the mid- to deep levels of the continental crust during the collision between Eurasia and Arabia–Africa since the Cretaceous (Fig. 1). Although tectonic processes developed broadly synchronously, it is appropriate to exclude the Himalayan orogeny here because it resulted from the collision of India with Eurasia, and on closer inspection, the tectonics and the time lines of orogenic processes are quite different. In its broadest sense, the term “Alpine terrane” is used by some as a generic term for all Tertiary metamorphic belts worldwide. Here we will follow the more common definition: the mountain belts situated in south–central Europe extending in the southeast as far as the Persian Gulf, with an occasional aside to processes occurring in insights developed for mountain belts elsewhere.

Much of the central and southern Eurasian continental crust shows evidence for severe alteration during the Variscan orogeny, roughly spanning the time period of ca. 380–300 Ma. In the southern

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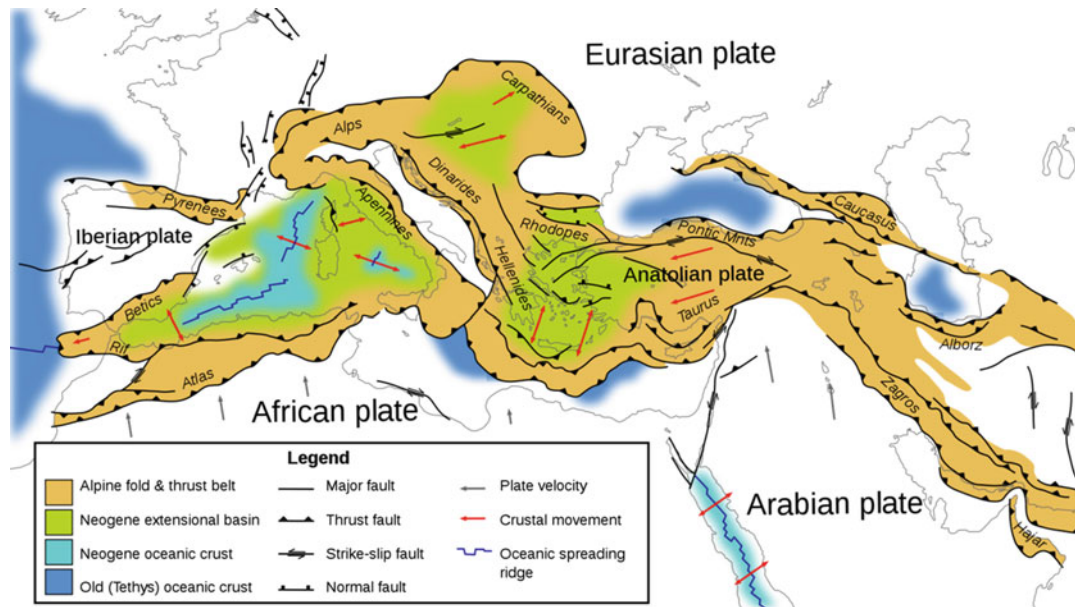


Fig. 1 The Alpine fold belt in southern Europe and the Middle East (Published with permission of the author, H.W. Goede)

Arabian–African continent, the crystalline basement consists of rocks of ca. 500–700 Ma, which belong to the Pan-African event in the east, and Maghrebien rocks of Variscan age in the west. The Rif mountains in northern Morocco form the southern extent of an Alpine orogenic arc bordering the Alboran Sea.

Between the main northern and southern blocks, during the Mesozoic, there were smaller blocks of continental crust that were exposed to an extensional regime in Triassic and Jurassic times (e.g., Manatschal 2004). Extension at that time was accompanied by mafic underplating and severe alteration of the continental lower and middle crust between ca. 280–200 Ma. Evidence for this period of pre-Alpine evolution in this domain can be found in the Austro–Alpine thrust sheets in Eastern Switzerland and Austria, in the bordering regions of northern Italy, in the Pyrenees, and in the Catalan coast ranges. Rocks of this age in the Southern Alps, south of the Insubric line separating the Internal Alps in the north from the Southern Alps, are interpreted as forming the thinned margin of the Adria micro-continent (Bertotti et al. 1999). In conclusion, although in quite a substantial part of the Alpine orogen metamorphic rocks of Triassic and Jurassic age are exposed, tectonic analysis suggests strongly that these rocks were formed during a phase of rifting that preceded the phase of continental collision that formed the Alps.

The collisional phase that initiated the Alpine orogeny was accompanied by deep subduction of the continental crust, and much current research is focused on finding out when these phases of deep subduction occurred. In much of the Alpine domain, Paleocene–Eocene ages are found. In the west, in the Betic Cordillera, subduction-related metamorphism is possibly as young as the Oligocene, but in parts of eastern Europe, in the Eastern Alps, in the Julian Alps of Slovenia, and in the internal Hellenides around the Ossa and Olympos ranges, Cretaceous ages of 90–100 Ma are associated with the blueschist- and eclogite-forming events.

In several sectors of Alpine Europe, the phase of deep subduction was followed by a phase of medium- to high-temperature metamorphism at mid-crustal depths during the Miocene; examples can be found in the Betics, the Lepontine domain of the Swiss Alps, the Tauern window in Austria, and the Greek Cyclades. Granitoid magmatism and associated volcanics are found in the peri-

Adriatic domain of the southern Alps in northeast Italy, with ages of ca. 45 Ma for the Adamello (Schoene et al. 2013), 32–24 Ma for the Bergell (Blanckenburg 1992), and ca. 21 Ma for the Pohorje granites of Slovenia (Fodor et al. 2008). In the Greek Cyclades, granites intruded during the Miocene (Altherr and Siebel 2002).

Active volcanism related to subduction can be found in the Alboran domain in the west, in the Calabrian arc north of Sicily, and in the Hellenic arc, where Santorini is the most prominent volcano. Late Miocene to recent potassic and ultrapotassic volcanism is found in the Betics in southern Spain and in the Roman province in central Italy.

Historical Perspectives

While the early efforts of dating the crystalline rocks of the Alps proved quite effective in outlining the broad age groups for the rocks found in the Alps, the general complexity of the Alps as an orogen, and the fact that initially quite large samples needed to be used for isotopic analysis, prevented the early workers from obtaining a true picture of the Alpine geochronology. However, new insights from mineralogy and petrology on the one hand, and tectonics on the other, helped in refining the image that we have of Alpine processes. The early division in Eo-Alpine, Meso-Alpine, and Neo-Alpine periods for rocks yielding Mesozoic, Paleogene, and Neogene ages has largely been abandoned in the light of a better understanding of Alpine tectonics.

Probably the most important result of the early efforts of understanding Alpine geochronology was the observation that minerals when dated with the K/Ar method yielded systematically younger ages when compared with their Rb/Sr ages (e.g., Jäger 1979). This observation, combined with the subsequent realization that minerals that were formed during the ca. 320–350 Ma Variscan yielded Alpine ages in a section with increasing overprinting temperatures during the Alpine orogeny, led to the understanding that the isotope systems in minerals such as muscovite and biotite displayed open- or closed-system behavior with respect to the radiogenic isotopes formed from radioactive decay in these minerals. The Berne geochronology group was in an ideal situation to make this observation because Swiss petrologists using the results from experimental petrology had come quite far with assigning temperature estimates to the prograde temperature sequence in the Swiss Alps from the external units in the north and northwest to the internal zones in the south (e.g., Frey et al. 1974). As a result of this early work, the transition from closed to open system in the K/Ar and Rb/Sr systems of common rock forming minerals such as muscovite and biotite could be assigned a quantitatively determined temperature, for which the Berne group used the term “blocking temperature” (Jäger 1979). As the blocking temperatures of minerals appeared to be intrinsic properties, different temperatures could be assigned to the age of minerals; it became possible to determine quantitative cooling rates for rocks cooling after metamorphism.

At the time that the Berne team was quite far advanced with calibrating the temperatures for the transition of closed- to open-system behavior by comparison with temperature estimates from thermobarometry, other researchers focused on experimental determination of diffusion rates for radiogenic isotopes such as isotopes of Sr and Ar in minerals (e.g., Mussett 1969; Giletti 1974a; b). The mathematical equations describing diffusion in objects with simple shapes such as a sphere or a cylinder can be derived under the assumption that diffusion of particles and heat obey the same physical laws and hence can be described using similar mathematical equations. The diffusion equation allows calculation of loss of, for example, radiogenic daughter isotopes from minerals with time at a range of temperatures but can also be used with some success to describe the diffusion of cations necessary to build new minerals as metamorphic reactions proceed. As an example, time

spans required to achieve a threshold value of 90 % loss of radiogenic daughter isotope are very long at low temperatures and become gradually shorter at higher temperatures, and full resetting can be expected when the time for 90 % loss of radiogenic daughter isotopes is in the same order of magnitude as the time span of the metamorphic overprinting. The diffusion equation also predicts a grain size effect, with larger grains taking longer to lose all radiogenic daughter isotopes. Finally, the mathematics of diffusion requires that once the diffusing isotope has diffused out of the crystal, it is effectively taken away and will not increase the concentration of isotopes at the surface of the crystal occupying the intergranular pore space. Some of the complexities in the interpretation of age results in young mountain belts can be attributed to the fact that not all of these boundary conditions are always fulfilled. In the next section examples will be given of such complexities in the interpretation of age data in young mountain belts.

Complexities in Interpretation

In Alpine metamorphic terranes, isotope geochronology can be particularly powerful because in this age range (generally processes take place during the period younger than 66 Ma) the resolving power of the isotopic dating techniques is high, and it can be expected that different phases of metamorphic overprinting can be resolved. In areas that have experienced high temperatures and where recrystallization has gone to completion, results of isotopic dating can be interpreted as recording cooling, and the ages that are thus obtained are recording closure temperatures (see chapter ► [Metamorphic Terranes](#)). Dodson (1973) defined the closure temperature in a cooling system as the temperature of the system at the time defined by its measured isotopic age. Using the mathematics of diffusion, Dodson demonstrated that a closure temperature can be calculated when an activation energy, E_a , and diffusion constant, D_0 , for a mineral phase are known. A closure temperature is defined for mineral phases that initially do not contain any radiogenic daughter isotope, and the actual value depends on the radius of diffusion and rate of cooling of the rock. In an ideal crystal, the radius of diffusion is likely to be equal to the grain radius, but in deformed or twinned crystals, the diffusion radius is more likely to be the radius of the subgrains formed during twinning or deformation and can be substantially less than the original grain radius. Further, while based on the mathematical equations for diffusion, Dodson's closure temperatures are implicitly defined only for the situation where the concentration of radiogenic daughter isotope at the grain boundary is zero. In reality, finite concentrations of radiogenic daughter may occur especially in cases where the mobility in the intergranular space is decreased. Examples of the simple case of rocks cooling from high temperatures (>ca. 600 °C) can be found in every Alpine metamorphic terrane that reached high temperatures during metamorphic overprinting. Examples of cases where the boundary conditions for Dodson's closure temperature definition are violated can be found in most mountain belts in the regions where metamorphic temperatures were lower (<ca. 500 °C), when minerals formed at a temperature below their closure temperature, or where minerals were not fully reset and still contain radiogenic daughter isotope from the period preceding the studied metamorphic event. The boundary conditions for calculating a closure temperature may also be violated during high-pressure and ultrahigh-pressure metamorphism when rock porosity is severely decreased, thus effectively preventing transportation of radiogenic daughter isotope out of the system once the first step of diffusion out of the crystal lattice has occurred.

Examples

In a study of the metamorphic evolution of the Mulhacen complex in the Betic Cordillera in southern Spain by De Jong et al. (1992), muscovites yielded uniform ages in the range of 11–12 Ma, whereas observation of the structures in the rocks suggested a fairly complex tectonic evolution. The uniformity in K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ ages suggested that much of this tectonic complexity predated the high-temperature event. In order to shed additional light on this history that could not be measured from analysis of normal matrix muscovite, a megacryst of ca. 5 mm diameter, i.e., some 20 times the size of the matrix, was measured using a spot heating laser technique. Relying on the prediction of diffusion theory that diffusion loss is in part controlled by the grain radius, it was expected that a signal predating the pervasive 11–12 Ma event could be found. From spot analysis using an argon ion laser, a concentric pattern of ages increasing towards the center of the grain was found, indicating that the megacryst was at least 27 Ma old. This can be taken as confirmation that grain size and diffusion radius define isotopic closure: the smaller grains record the younger cooling age, whereas a larger grain yielded a much older cooling age.

An important observation was made by Baxter et al. (2002), who worked in high-temperature metamorphic rocks in the Simplon area, part of the internal zone of the Swiss Alps. Here, it appeared that there was a systematic bias in $^{40}\text{Ar}/^{39}\text{Ar}$ ages of biotites that were measured from mica schists and biotites in meta-basalts. As the rocks were interlayered in a relatively small area, it could be safely assumed that their metamorphic histories were the same. Also the grain sizes were in the same range. Yet the ages obtained from the minerals from the meta-basalt were systematically higher than those found from the mica schists. The interpretation was that the diffusivity of radiogenic daughter isotope was less in the meta-basalt and higher in the mica schist. A lower diffusivity in the intercrystalline pore space may imply that a substantial concentration of radiogenic daughter isotope could be maintained in the pore space during the peak temperatures of metamorphic overprinting. Isotopic closure is firmly based on diffusion theory that assumes that the concentration of radiogenic isotope in the pore space remains zero at all times, i.e., when radiogenic daughter isotope is removed from the crystal by volume diffusion, it is also removed from the system. When due to lower diffusivity a higher concentration of radiogenic daughter isotope can be maintained, this would result in the preservation of systematically higher isotopic ages.

At metamorphic temperatures that are lower (i.e., < ca. 600 °C) and at metamorphic pressures that are higher, the complexity of the preserved isotope signal is expected to increase; at lower metamorphic temperatures, isotopic resetting may not go to completion as at these temperatures the system remains below the closure temperatures of various minerals (Warren et al. 2012). At increased burial depth, the porosity of the rock will decrease, and with the concomitant decrease in diffusivity, the concentration of radiogenic isotopes at the grain boundaries will increase. As a result of these elevated concentrations of radiogenic isotopes, full resetting of geochronometers may not be achieved.

As a result accumulation of radiogenic daughter isotope may start at different times in different crystals of the same mineral phase. Complex crystallization histories potentially can be resolved, with a combination of detailed microstructural characterization and access to single crystal or spot dating techniques as demonstrated by Beltrando et al. (2008). Another level of complexity is added in the situation where a preexisting mineral assemblage is overprinted. In an early study of this situation, Wijbrans and McDougall (1986) demonstrated that phengites formed during early high-pressure metamorphism at or before ca. 45–50 Ma in Naxos, Greece, were progressively overprinted by younger more muscovitic phengites and true muscovites during a younger metamorphic phase that ranged in peak temperature from >450 °C to ca. 700 °C in the period 15–11 Ma. It could be

demonstrated in this case that as long as early phase phengites remained present in the rock, an elevated age signal was found. This observation underlined the conclusion that recrystallization is the faster, more effective mechanism to reset the isotope system. In addition, it was argued that given the observation that full resetting of the early phengites was not observed, it should follow from diffusion theory that the duration of the subsequent thermal pulse that caused the high-temperature mineral assemblages may have been rather short.

In a study of the blueschist – greenschist metamorphism of the internal Hellenides, Lips et al. (1998) by careful selection could isolate and date various phases of blueschist phengites and younger greenschist muscovites in an age range between 90 and 40 Ma, including an example of a Variscan orthogneiss that exhibited ca. 320 Ma protolith muscovites. They also found overprinting of Alpines phengites with ages of ca. 65 Ma. At no time since the Cretaceous were metamorphic temperatures high enough to fully reset the isotope systems of the white micas; complete ranges in ages from Variscan protolith ages to late stage Alpine greenschist facies ages were preserved.

In the internal Western Alps during Alpine collision, high- and locally ultrahigh-pressure metamorphic conditions were reached during the Paleocene–Eocene, as confirmed by U/Pb zircon dating, Sm/Nd dating, and Lu/Hf dating of garnet-bearing mineral assemblages (Rubatto and Hermann (2003), Lapen et al. (2003)). The K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ records of phengites and muscovites in these areas yielded a complex picture with ages in the range of ~40 Ma to 120–200 Ma, with outliers as high as ~300 Ma (e.g., Scaillet 2002). The simplest interpretation would be to accept the ca. 40 Ma ages as consistent with the U/Pb and Sm/Nd and Lu/Hf data, and everything older is an artifact caused by excess argon. However, the protolith age of the orthogneiss Variscan granite with ages up to the range of ca. 300 Ma would be consistent with a Variscan protolith history and might suggest inheritance of an older argon signal that is preserved despite Alpine tectonism and metamorphism in the Eocene.

Much of the complexity in the interpretation of K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ age data is caused by the mobility of ^{40}Ar in natural rock systems. Formed by the decay of ^{40}K , ^{40}Ar is a noble gas. As a neutral atom, argon is not a constituent part of a crystal lattice of the mineral in which it formed. The mobility of argon in minerals is best described by a volume diffusion mechanism, for which a pre-exponential diffusion constant D_0 and activation energy E_a can be determined experimentally. Although volume diffusion in pristine, undeformed crystals is likely to be a very slow process, diffusion in a compact aggregate of minerals along defects and grain boundaries is considered to be a faster process as the permeability along the grain boundaries is higher than within the crystal itself (Lee 1995). Porosity may vary from very low to high, as pore space may range from very low volume without any interconnection to full interconnection allowing advection of a fluid through the rock. In order to release the radiogenic argon trapped within the crystals, the slowest mechanism is via volume diffusion, whereas other processes such as grain boundary diffusion and recrystallization are likely to be much faster, as the bonds between the ions forming the crystal lattice are broken in the latter process, and trapped argon can be released via grain boundaries (Wijbrans and McDougall 1986).

The interpretation of dating results from rocks from Alpine terranes thus may be complicated by the degree of mobility of argon during metamorphic overprinting. When ages are found with K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating that are older than expected, the system contains extraneous argon. For practical purposes, two common forms of extraneous argon can be defined: excess argon that is released into the system when potassium-bearing minerals break down and inherited argon, which is radiogenic Ar that was incorporated in the lattice of a preexisting mineral. In the case of inherited argon, traces of a prehistory may not have been fully erased during overprinting and can be used in favorable cases to further constrain the thermal evolution of the rock.

Summary and Conclusion

In the Alpine orogenic belt in central and southern Europe, rocks were exposed to elevated temperatures and pressures caused by tectonic processes of subduction and collision of continental crustal blocks during closure of oceanic basin such as the Tethys and Paratethys basins. These processes occurred predominantly during the Paleogene and Neogene and in some sectors as early as the Late Cretaceous. Earlier processes recorded in the rocks appear to be related to the processes predating the Alpine subduction and collision orogen. Evidence for earlier processes and artifacts caused by the mobility or in cases the lack of mobility of radiogenic daughter isotopes add to the complexity of interpreting isotopic age data in the low-temperature and high-pressure domains in mountain belts.

Because metamorphic processes in the Alps occurred during a relatively young period of Earth's history, much of the tectonic evolution causing metamorphism can be resolved in time. As a result many of the mechanisms of behavior of isotope systems were first described in the Alps.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Metamorphic Rocks \(Sm-Nd\)](#)
- ▶ [Metamorphic Terranes \(K-Ar/Ar-Ar\)](#)
- ▶ [Minerals \(Ar-Ar\)](#)
- ▶ [Structural Fabrics \(K-Ar/Ar-Ar\)](#)

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Metamorphic Terranes ($K\text{-Ar}/^{40}\text{Ar}/^{39}\text{Ar}$)

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Synonyms

[Metamorphic basement](#); [Metamorphic belts](#)

Definition

Metamorphism in its widest sense refers to processes of alteration of rocks within the Earth crust and mantle that cause recrystallization of an original mineralogy to form new minerals that are thermodynamically stable at depth and thus reflect in their chemistry and mineralogy the changed physical conditions of pressure, temperature, stress regime, and partial pressures of volatile phases such as H_2O , CO_2 , CH_4 , and others during the time of recrystallization.

Metamorphism covers a spectrum from partial recrystallization to complete recrystallization. Partial recrystallization may reflect processes within a single cycle (pluri-facial metamorphism) or multiple cycles of metamorphism spaced out in time (poly-metamorphism). Retrograde metamorphism reflects often partial recrystallization after peak metamorphism.

Terranes are units of rocks at the crustal scale that share common geological features and a common geological history.

Metamorphic terranes therefore are terranes that consist largely of metamorphic rocks that share a common history of burial, metamorphism, and exhumation.

Introduction

Much of the continental middle and lower crust consists of metamorphic rocks. Much of the upper mantle, as far as we can tell from mantle rocks exposed at the Earth surface in ophiolite units and from xenoliths brought up from the upper mantle by magma transport, is also metamorphosed. In the oldest nuclei of continental crust, preserved Archean cratons, metamorphism may range from very low grade in the greenstone belts to granulite grade in the basement gneiss terranes. From the early Proterozoic onward, metamorphic terranes are often found in long and narrow belts, reflecting the fact they formed along the margins of plates of continental crust or by continent—continent collision processes (Fig. 1).

The general objective of geochronological analysis of metamorphic terranes is to shed light on the age of the protoliths and to place time constraints on the prograde (burial) path, peak metamorphic temperature (T) and pressure (P) conditions, and cooling after the peak of the metamorphic event, often during exhumation of the rocks (Fig. 2). Metamorphism is the alteration

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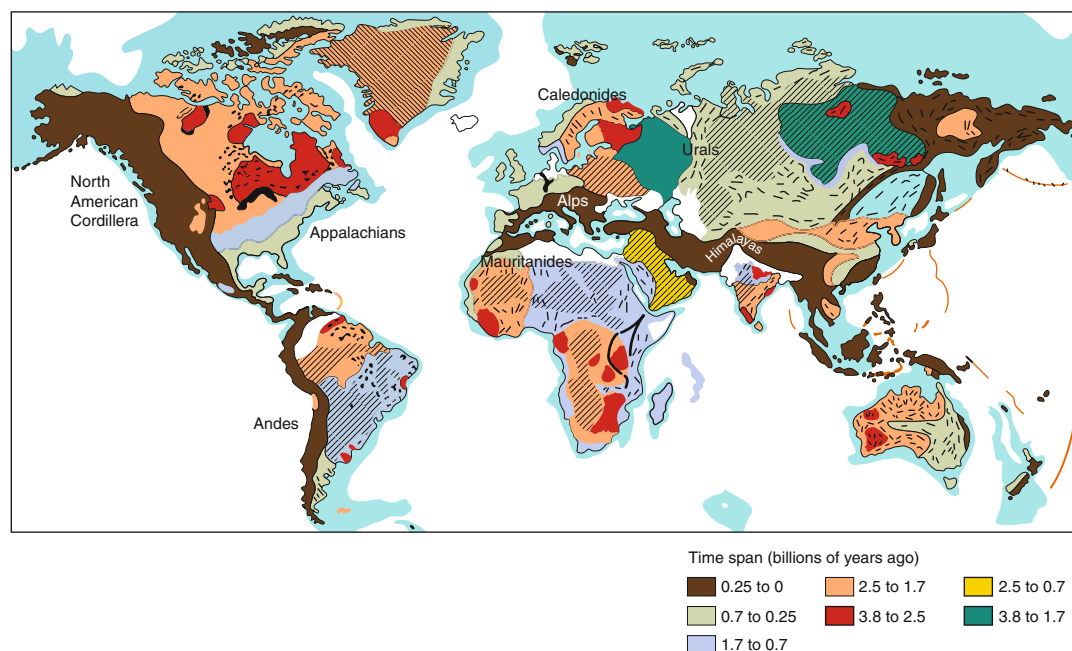


Fig. 1 Global distribution of orogenic belts containing metamorphic terranes, highlighting linear belts from ca. 2.0–1.7 Ga

of the mineral content of rocks caused by either changing PT conditions during burial caused by subduction or continental collision and associated rock deformation events or by heat or fluid advection as is, for example, the case when granites intrude into higher crustal levels or when basaltic magma underplates the continental crust.

Peak temperatures reached during metamorphism may range widely from ca. 400°C for the prehnite–pumpellyite facies to temperatures in excess of 900–1,000°C for the ultrahigh-temperature domain of the granulite facies. Metamorphic pressures recorded in crustal rocks in extreme cases are known to have exceeded lithostatic pressures consistent with what can be expected for normal crustal thicknesses by at least three times, suggesting either that during subduction or collision events, crustal rocks may have been pushed to great depths or that tectonic stress may build up to values substantially exceeding the normal lithostatic pressure. Minerals diagnostic for ultrahigh pressure include coesite and diamond that form at pressures in excess of 2.5 and 3 GPa, respectively.

For slowly cooling metamorphic terranes, the K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological techniques record ages usually interpreted as corresponding to the Ar closure temperatures (Dodson 1973) of their constituent minerals. Although closure temperature is dependent on the grain size of the minerals, such ages typically reflect the time at which the rocks cooled below ca. 500–550°C for metamorphic hornblende, ca. 150–400°C for K-feldspars, 360–420°C for metamorphic muscovite, and 280–330°C for metamorphic biotite, respectively. The exact “closure” temperatures for which timing information is obtained may be more difficult to determine, as they depend on cooling rate and radii of the crystal domains over which diffusion occurs. The determination of the exact closure temperature may be hindered by partial recrystallization or deformation, as under such conditions non-volume diffusion processes may have altered the age of the mineral.

As a consequence, the K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ techniques can typically be used to measure the age of metamorphic peak temperatures in those areas where the peak temperature has not exceeded

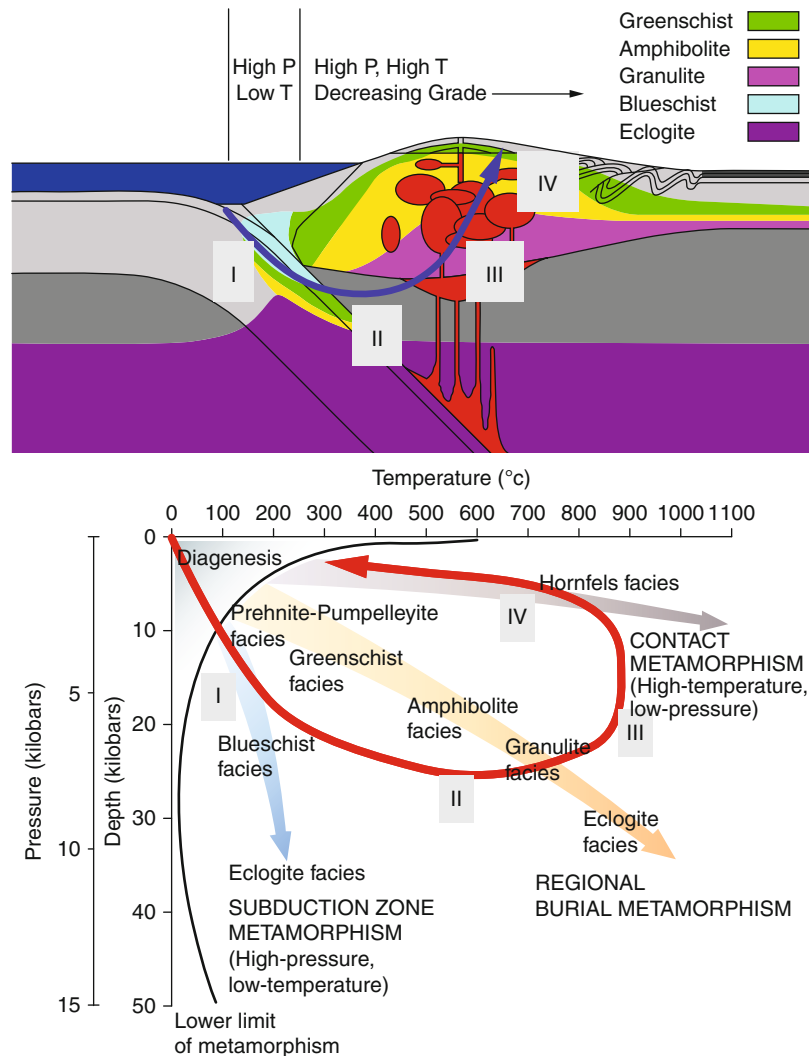


Fig. 2 Section through a convergent margin and PT diagram showing the PT fields of the various metamorphic grades. *I*, prograde path; *II*, peak metamorphic pressure; *III*, peak metamorphic temperature; *IV*, retrograde path

temperatures of 400–550°C for considerable amounts of time, i.e., at the prehnite–pumpellyite, greenschist, blueschist, and lower amphibolite facies metamorphic grades (Warren et al. 2012).

In higher-grade metamorphic terranes, the K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods are useful to constrain the cooling path of the rocks to temperatures below the closure temperatures of hornblendes, muscovites, biotites, and K-feldspars, respectively. The K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods can be applied to a wide range of K-bearing minerals and rocks, although hornblendes, micas, and K-feldspar are the most widely used minerals used for dating in metamorphic terranes.

Historical Perspectives

The K–Ar method has been in use since the 1950s, whereas the $^{40}\text{Ar}/^{39}\text{Ar}$ method was first developed in the mid-1960s and has since become the preferred method for dating by the ^{40}K – ^{40}Ar isotopic system. Whereas the K–Ar technique was quite successful in dating of volcanic and simple igneous rocks, it became apparent that the method did not always work well in old,

Table 1 Closure temperature ranges

Mineral	Temperature range (°C)
K-Feldspar	~150–400
Biotite	~280–330
Muscovite	~360–420
Hornblende	~500–550

Modified from Johnson and Harley (2012)

complex Precambrian metamorphic basement rocks, where consistently younger ages were often found in rocks that had demonstrably complex extended tectonic histories (e.g., Kinny et al. 1990). Moreover, researchers working in younger, Alpine metamorphic rocks found that in rocks and minerals dated with both the Rb/Sr dating technique and the K–Ar dating technique, the K–Ar technique often yielded systematically younger ages (e.g., Armstrong et al. 1966). This observation was used with advantage, when combined with estimates for metamorphic temperature deduced from the rocks used for dating, to estimate an empirical temperature reflecting the opening and closing of the isotopic system, a so-called “blocking” temperature. The blocking temperature for a mineral was defined as the temperature at which the isotopic system was reset during metamorphic overprinting, yielding for the first time temperatures above which isotopic ages could not be preserved (Jäger 1979). Clearly, under such extreme conditions, the K–Ar technique may only yield a partial answer to the question of timing of the tectonic evolution of the crust.

During this same period, the $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating method was used to derive diffusion parameters for the diffusion of argon through the crystal lattices of various K-bearing minerals. Results of these first attempts to measure diffusion rates in hydrous minerals such as biotite and hornblende were unreliable as the mineral structures become instable due to dehydration reactions in vacuo (Mussett 1969; Hoffmann 1979). When such minerals were kept stable at high temperatures under hydrothermally controlled pressures, the diffusion results were more predictable (e.g., phlogopite, Giletti 1974; hornblende, Harrison 1981). The experimentally determined diffusion parameters, i.e., the pre-exponential coefficient, D_0 , and activation energy, E_a , could thus be used to predict diffusion loss from the crystal lattice of minerals at elevated temperatures. This approach led to the definition of a closure temperature (Dodson 1973), formally defined in a system cooling from high temperature as the temperature of the mineral at the time determined by its isotopic age. In contrast, a blocking temperature refers to an empirically calibrated temperature of resetting of isotopic ages in minerals. Although very powerful for the description of cooling systems, the use of closure temperatures to describe the loss of isotopic daughters during reheating is more complex, because in practice when the original mineral remains stable, the duration of the overprinting pulse, grain size, and degree of deformation play a role in affecting the age of the rock or mineral. Several researchers have attempted to model diffusion numerically using modified heat flow codes (Lister and Baldwin 1996; Wheeler 1996); this approach is particularly useful to test the effects of various parameters that may influence resetting by diffusion.

Diffusion is typically a rate-limiting process, so to be measured accurately a diffusion experiment needs to be carried out within the mineral’s stability field. Because the amounts of diffusion loss during experiments are very low, diffusion experiments present many analytical challenges; the results of several carefully controlled experiments are given in Table 1. An important consideration is that Ar diffusion may result from different mechanisms that occur simultaneously in minerals. In a perfect crystal lattice, diffusion of argon will proceed by a point defect process (also commonly known as volume diffusion); the large argon molecule has to push lattice ions out of the way in order to migrate through the lattice. Because the neutral argon molecule cannot substitute

for the lattice-forming ions, an exchange mechanism for Ar diffusion is not likely to occur. However, deformed crystals will contain defects or dislocations of the crystal lattice. Such defects will also diffuse through a crystal lattice at elevated temperature. Dislocation-driven diffusion and the point defect diffusion process are likely to have different diffusion constants and activation energies (Lee 1995) and thus may lead to varying estimates for closure temperatures. These considerations have led some researchers to suggest that true volume diffusion is so slow that it is not an effective means of mass transport, even at geological timescales at temperatures commonly occurring during metamorphism (Villa 1998).

Under the assumption that anhydrous minerals such as K-feldspar do not undergo phase changes during laboratory heating in vacuum, and hence argon loss during stepwise heating will follow a volume diffusion-governed process, it was argued that it is possible to model complex patterns of apparent age spectra assuming a finite number of sub-crystal sizes with different radii for diffusion (Lovera et al. 1989). Such a model could then be used to imply a discrete cooling history at geologically relevant time scales. Another approach, using higher-temperature geochronometers and lower-temperature geochronometers based on other isotopic decay systems such as U/Pb, Sm/Nd, and Rb/Sr, has been very useful in the quantification of crustal evolution studies (Kalt et al. 2000).

General Description

The $^{40}\text{Ar}/^{39}\text{Ar}$ method can be applied successfully in metamorphic terranes provided that the temperature history is well known from thermobarometric studies, thus linking the measured ages to the PT history of the rock. In this section, some examples of different time slices of Earth history will be discussed.

The oldest rocks on Earth dated successfully with the $^{40}\text{Ar}/^{39}\text{Ar}$ method are from the Kaapvaal and Pilbara cratons, both now situated in the southern hemisphere. In the Kaapvaal craton, komatiites from the Onverwacht Group in Barberton were dated at 3.45 Ga by Martinez et al. (1984), and the ages were interpreted to record the timing of lower-greenschist facies overprinting of the volcanics shortly after deposition. Layer et al. (1998) obtained an age of 3.18 Ga on the Nelshoogte pluton. In the Pilbara craton of Western Australia, Wijbrans and McDougall (1987) published hornblende ages as old as 3.2 Ga from the Western Shaw greenstone belt and demonstrated that within the adjacent granitoid domes, amphibolite facies metamorphism continued until 2.95 Ga. Subsequent work (Davids et al. 1997; Zegers et al. 1999) showed that in the Pilbara craton, also 3.4 Ga rocks have been preserved in the greenstone belts.

The metamorphic evolution of several Proterozoic metamorphic terranes has been studied using the $^{40}\text{Ar}/^{39}\text{Ar}$ method. Studies have focused on the metamorphic evolution of the early Proterozoic Arunta block in Australia and the eastern part of the Baltic shield in Scandinavia. Early Proterozoic mobile belts are relatively narrow metamorphic terranes in the Archean cratons, for example, the Limpopo belt in Southern Africa, the Capricorn belt in Western Australia, and the Nagsugtoqidian belt in Greenland are examples of such terranes that experienced metamorphic overprinting in the period ca. 2,000–1,700 Ma. The younger Grenville metamorphic event is most pronounced in North America characterized by ages in the range 1,200–800 Ma. Grenville-aged rocks are widespread and have been found in the Baltic Shield and in South America, where they can be straightforwardly linked to the core Grenville of North America; Grenville-age rocks also occur in Asia.

Younger Proterozoic metamorphic terranes can be found in the southern continents that formed part of Gondwana at a later stage of their history. For example, Pan-African metamorphic belts occur as relatively narrow mobile belts of ca. 500–600 Ma in age, and Pan-African age mobile belts occur, for example, in Northeast Africa, Egypt and the Sinai, Southeast Africa, Madagascar, India, and Western Australia.

Early Paleozoic metamorphic terranes occur in the Atlantic domain, in the Caledonian belt of western Scandinavia, eastern Greenland, and Eastern North America. HP and UHP rocks of the same age occur in the Urals and the Central metamorphic belt of China, whereas in southeastern Australia the Ordovician Lachlan fold belt is a low-grade slate belt.

Very young metamorphic terranes have been described tectonic systems that are active at present, such as the case of ongoing continental collision in, e.g., the Karakorum (Zeitler 1985), South Island, NZ (Chamberlain et al. 1995), and the D'Entrecasteaux Islands off the coast of Papua New Guinea (Baldwin et al. 2004), where Pliocene UHP rocks are exposed.

Summary and Conclusion

Much of the continental crust exposed within the continental interiors consists of metamorphosed rocks. These rocks can be conveniently grouped in terms of the age of metamorphism as recorded by common $^{40}\text{Ar}/^{39}\text{Ar}$ geochronometers such as K-feldspar, biotite, muscovite, and hornblende. Such a division illustrates the evolution of the continental crust through time from the early Archean exposed in the continental interiors to the youngest metamorphic rocks found in the rapidly exhumed rocks at the continental margins. Metamorphic rocks are important in that they often constitute the only record of evolution of the continental crust and bear evidence for tectonic processes in the geological past.

Cross-References

- ▶ [Alpine Terranes \(K–Ar/ \$^{40}\text{Ar}/^{39}\text{Ar}\$ \)](#)
- ▶ [Metamorphic Events, \(Rb–Sr\)](#)
- ▶ [Metamorphic Events, \(Sm–Nd\)](#)
- ▶ [Tectonic Processes, \(Thermochronology\)](#)
- ▶ [Uranium-Lead, Metamorphic Rocks](#)

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Lu-Hf Dating: The Lu-Hf Isotope System

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Definition

The radiogenic isotope applications of the Lu-Hf system utilize variations in ^{176}Hf resulting from the radioactive decay of ^{176}Lu to ^{176}Hf and variations in the Lu/Hf ratios in rocks and minerals. It is used both in geochronology, primarily in rocks containing a high Lu/Hf phase, and in tracer isotopic applications, to track the chemical evolution of the Earth and other solar system materials and to constrain the sources of magmas and sediments.

Introduction

The Lu-Hf isotope system, with applications to geo- and cosmochemistry, was first investigated in the early 1980s (Patchett 1983b; Patchett and Tatsumoto 1980a, b, c, 1981) following the successful implementation of the Rb-Sr and Sm-Nd isotope systems several years earlier.

There are some obvious similarities between the Lu-Hf and Sm-Nd isotope systems and, as a result, they have long been used in concert in a wide range of studies (e.g., Beard and Johnson 1993; Blichert-Toft and Albarède 1997; Johnson and Beard 1993; Patchett and Chauvel 1984; Patchett 1983b; Salters and Hart 1991; Vervoort and Blichert-Toft 1999; Vervoort et al. 1999). In these two systems all elements are lithophile and refractory with high condensation temperatures. Because of these characteristics it has long been assumed that their abundances in the Earth can be approximated by chondritic meteorites (see discussion below). In addition, all elements in these systems behave incompatibly during melting and are concentrated in the melt over the residual solid. In both systems, the daughter element (e.g., Nd, Hf) is more incompatible than the parent, leading to lower Sm/Nd and Lu/Hf ratios in the melt than the residual solid. As a result, the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in magmatic rocks are highly correlated (e.g., Chauvel et al. 2008; Johnson and Beard 1993; Patchett 1983a; Salters and Hart 1991; Vervoort and Blichert-Toft 1999). Both Lu and Hf are highly immobile and insoluble and, as is the case with the Sm-Nd system, are thought to be resistant to perturbations and retain their isotopic information through significant degrees of alteration and metamorphism.

In the case of the Lu-Hf isotope system, the parent is the heaviest of the rare-earth elements (REEs) and has broad geochemical similarities with all other +3 valence REEs. The daughter element, however, is not an REE, but a high-field-strength element (HFSE) with a +4 valence and, as such, can behave much differently than the REEs. These differences can confer some advantages to the Lu-Hf isotope system for both geochronology and tracer isotopic work as will be discussed below.

Although the Lu/Hf ratio is fractionated during magmatic processes, the degree of this fractionation, as is the case for Sm-Nd, is not very large. This results in small variations in Lu/Hf ratios between not only rocks within a comagmatic suite but also for most mineral phases within individual

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rocks. This lack of parent/daughter variation severely limits the application of the Lu-Hf chronometer, much as it does for the Sm-Nd isotope system. Therefore, whole-rock Lu/Hf isochrons of truly comagmatic suites of rocks either have too limited variation in Lu/Hf ratios to provide precise ages or, if there is a significant Lu/Hf variation, chances are the suite of rocks used in creating the isochron was not truly comagmatic. There are a few phases, however, with high affinity for Lu, which make them highly useful in geochronology in both magmatic (e.g., apatite) and metamorphic (e.g., garnet, lawsonite) rocks. In addition, some other phases (particularly phases with Zr or Ti as stoichiometric constituents) have strong affinities for Hf (e.g., zircon, baddeleyite, rutile), which make them useful in tracer isotopic studies – especially when used in conjunction with the U-Pb geochronologic information from these mineral phases.

Although the Lu-Hf system was introduced to the geochemical and cosmochemical communities in the 1980s, analytical challenges limited the widespread use of this technique until the late 1990s. The reason for this is that Hf has a very high first ionization potential (6.83 eV, Lide 2003), which prevented easy and routine analysis of Hf isotopes using thermal ionization mass spectrometry (TIMS). As a result there were only a few practitioners using this system in the 1980s and much of the 1990s. These difficult analyses utilized specialized techniques and required considerable amounts of Hf for the analyses to be successful. This all changed with the advent and development of the multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS), which combined the efficient ionization of Hf using an ICP ionization source with the high precision analysis afforded by multi-collector mass spectrometry (Blichert-Toft et al. 1997; Walder and Freedman 1992). This revolutionized the use of the Lu-Hf isotope system for geochronology and tracer isotope applications by allowing the routine analysis not only of Hf isotopes in general but also of much smaller amounts of Hf. This made several important things possible. *First*, it allowed for the more precise and accurate determination of the ^{176}Lu decay constant (Scherer et al. 2001; Söderlund et al. 2004). *Second*, the new MC-ICPMS instrumentation also facilitated the analysis of high Lu-Hf, but Hf-poor, phases like garnet or apatite, which made the use of these phases for geochronology possible. *Third*, it also made it possible to analyze Hf-poor rocks such as chondritic meteorites, which allowed more accurate constraints to be placed on the chondritic Lu-Hf value (e.g., Bouvier et al. 2008). *Finally*, MC-ICPMS technology has made it possible to determine the Lu-Hf isotope composition in very small, Hf-rich phases such as zircon. This latter application, particularly when done in conjunction with U-Pb geochronology, has enjoyed an explosion of use in recent years (e.g., Amelin et al. 2000; Fisher et al. 2014; Gerdes and Zeh 2009; Kemp et al. 2010; Woodhead et al. 2004; Xie et al. 2008; Yuan et al. 2008).

Background

Lutetium is the heaviest of the rare-earth elements (REEs) and shares a +3 valence with the lanthanides as a whole. It also has an odd atomic number (odd number of protons; $Z = 71$), which, in part, makes it the least abundant of the REEs (67 ppb; McDonough and Sun 1995). Lu has two isotopes (Table 1): ^{175}Lu is stable, is an odd-even nuclide, and is the most abundant isotope (97.4 %); ^{176}Lu is an odd-odd nuclide, has low abundance (2.6 %), and is radioactive, decaying primarily to ^{176}Hf by beta decay. A small percentage (<3 %) of ^{175}Lu is reported to decay to ^{176}Yb by electron capture (Dixon et al. 1954) although Amelin and Davis (2005) establish an upper limit of 0.9 % based on combined electron capture and positron emissions.

Hafnium is the next higher element from Lu on the periodic table ($Z = 72$) and is a high-field-strength element (HFSE) sharing geochemical similarities with other Group IVB elements, most

Table 1 Isotopic composition of Lu and Hf

	¹⁷⁵ Lu			¹⁷⁶ Lu		
Ratio to ¹⁷⁶ Lu	37.666			1.0		
Atomic %	97.41			2.59		
Atomic weight	174.94079			175.94269		
Atomic weight Lu	174.96670 g/mol					
	¹⁷⁴ Hf	¹⁷⁶ Hf	¹⁷⁷ Hf	¹⁷⁸ Hf	¹⁷⁹ Hf	¹⁸⁰ Hf
Ratio to ¹⁷⁷ Hf	0.0086743	0.282160	1.0	1.467170	0.7325	1.886660
Atomic %	0.1613	5.2474	18.5972	27.2852	13.6224	35.0865
Atomic weight	173.940065	175.94142	176.943233	177.94371	178.945827	179.946561
Atomic weight Hf	178.485367					

notably Zr and Ti. It is relatively under-abundant in the Earth (0.28 ppm, McDonough and Sun 1995) but enriched in the continental crust (5.3 ppm, Rudnick and Gao 2003). It has six isotopes, five of which are stable (Table 1). One isotope, ¹⁷⁶Hf (5.20 %), is radiogenic and produced, in part, by beta decay of ¹⁷⁶Lu and, together with ¹⁷⁶Lu, provides the basis of the Lu-Hf chronometer. By convention the reference stable isotope for the Lu-Hf system is ¹⁷⁷Hf (18.60 %).

In order to determine accurate Lu and Hf concentrations and, most importantly, the precise ¹⁷⁶Lu/¹⁷⁷Hf ratios required for geochronology and calculating accurate initial ratios, the “isotopic dilution” technique is required. This technique involves the addition of measured amounts of tracers of known isotopic composition (highly enriched in ¹⁷⁶Lu and ¹⁸⁰Hf, typically, with some labs using ¹⁷⁸Hf). These tracers, or “spikes,” are generally mixed and precisely calibrated so that evaporative loss will not affect the precise determination of the parent/daughter ratios. These spikes are added to the sample solution following or during dissolution, equilibrated with the solution, and become part of the isotopic mixture of the sample. Ultimately the ¹⁷⁶Lu/¹⁷⁷Hf and ¹⁸⁰Hf/¹⁷⁷Hf ratios of the samples are measured to determine Lu and Hf concentrations and precise Lu/Hf ratios.

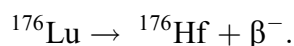
In order to correct for mass dependent fractionation during mass spectrometry (i.e., mass bias), the convention for the Hf isotope system is to normalize to ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325 (Patchett and Tatsumoto 1980b), the value that has been used since the early days of Hf isotope analyses. Mass bias for Lu isotopic analyses is complicated by virtue of the fact that Lu has only two isotopes, making internal normalization impossible. In the early TIMS era of Lu-Hf isotope measurements, the small degree of mass bias (~ 0.1 % per amu) was not as significant for the less stringent requirements of the Lu isotope dilution analysis. With the advent of the MC-ICPMS analyses, however, mass fractionation that is over an order of magnitude larger than TIMS necessitated an accurate mass bias correction. The current approach is to use a different element with at least one invariant isotope ratio and which has a similar mass bias response, such as Yb, to correct for mass bias in the Lu isotopic measurement. Because of the similarity of behavior of the REEs (particularly for adjacent REEs), it is often difficult to quantitatively remove Yb from Lu. The current practice employed in most labs is to remove the majority of the Yb (recall that Yb is an even element and so is much more abundant than the odd numbered Lu) and use the Yb isotope measurements to determine the mass bias and then apply this to the Lu measurement. This approach is somewhat complicated by the uncertain isotopic composition of Yb (e.g., Amelin and Davis 2005; Chu et al. 2002; Segal et al. 2003; Vervoort et al. 2004) and the fact that ¹⁷⁶Yb is a relatively abundant isotope (12.70 %) with the same mass as the ¹⁷⁶Lu spike. The interference of ¹⁷⁶Yb on the spike isotope, ¹⁷⁶Lu, requires that most of the Yb be removed from the sample. In detail there are probably small differences in the mass bias of Yb and Lu, and there are approaches to quantify these differences

(e.g., White et al. 2000). Despite all of these challenges, $^{176}\text{Lu}/^{177}\text{Hf}$ ratios in rock samples can probably be determined to ~0.2 % accuracy (Vervoort et al. 2004).

The Hf solution standard employed throughout the history of Hf isotope analysis has been JMC-475, a Hf metal obtained from Johnson Matthey Corporation (Patchett and Tatsumoto 1980b) with a currently accepted $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282160 (Vervoort and Blichert-Toft 1999). The JMC-475 Hf standard solution is available from the author on request.

Decay System Fundamentals

Lutetium-176 decays to ^{176}Hf by beta decay with a half-life of 37.12 Ga:



Only a small percentage (~1 %) of ^{176}Hf in rocks and minerals is radiogenic and produced in this way; the majority of ^{176}Hf is “common” Hf, produced primarily during nucleosynthesis. The radiogenic decay equation for the Lu-Hf isotope system describes how radiogenic ^{176}Hf in a rock or mineral will evolve over time:

$$^{176}\text{Hf}_{(p)} = ^{176}\text{Hf}_{(t)} + ^{176}\text{Lu}_{(p)} * (e^{\lambda t} - 1).$$

This expression shows that the ^{176}Hf present in a given sample today is a function of (1) the ^{176}Hf in that sample at some time, t , in the past; (2) the amount of radiogenic ^{176}Lu in that material; (3) the amount of time elapsed since formation; and (4) the decay constant. In practice, we reference these isotopes to ^{177}Hf , a stable isotope of Hf. Thus the equation above becomes:

$$^{176}\text{Hf}/^{177}\text{Hf}_{(p)} = ^{176}\text{Hf}/^{177}\text{Hf}_{(t)} + ^{176}\text{Lu}/^{177}\text{Hf}_{(p)} * (e^{\lambda t} - 1).$$

Therefore, the material with high Lu/Hf ratios, such as garnet, will generate proportionally more ^{176}Hf over time and evolve to higher $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. Conversely, the material with low Lu/Hf ratios, such as zircon, will produce proportionally little ^{176}Hf with time and so its $^{176}\text{Hf}/^{177}\text{Hf}$ ratios will increase only very slowly.

An important part of using these radiogenic equations for geochronology and for determining precise initial isotopic compositions is not only measuring the present-day ratios accurately but also knowing the decay constant precisely and accurately. The ^{176}Lu decay constant has been a source of uncertainty, however, and this has limited the full application of the Lu-Hf isotope system. The first determination of the ^{176}Lu decay constant for use in geochemistry and cosmochemistry was performed by Patchett and Tatsumoto (1980a) who determined an isochron on a collection of basaltic and cumulate eucrite meteorites. Using a presumed age of 4.55 Ga for the differentiation event for the eucrites, they determined a value for $\lambda^{176}\text{Lu}$ of $1.962 \pm 0.081 * 10^{-11} \text{ year}^{-1}$ with a corresponding half-life of 35.3 Ga. This value was later revised by Patchett (1983b) to $\lambda^{176}\text{Lu} = 1.94 \pm 0.07 * 10^{-11} \text{ year}^{-1}$ and a half-life of $35.7 \pm 1.4 \text{ Ga}$. This revised value was similar to a decay constant value of $1.93 \pm 0.03 * 10^{-11} \text{ year}^{-1}$ determined by physical counting experiments (Sguigna et al. 1982). The agreement between these results led, in part, to the use of the $\lambda^{176}\text{Lu}$ value of $1.94 \pm 0.07 * 10^{-11} \text{ year}^{-1}$ throughout the 1980s and much of the 1990s, with later studies (e.g., Blichert-Toft and Albarède 1997 and subsequent papers) using the Sguigna et al.’s

(1982) values. This early history of ^{176}Lu decay constant determinations is reviewed more thoroughly by Begemann et al. (2001).

The value determined for $\lambda^{176}_{\text{Lu}}$ changed dramatically following age comparison studies by Scherer et al. (2001) and Söderlund et al. (2004). Scherer et al. (2001) suggested a $\lambda^{176}_{\text{Lu}}$ value of $1.865 \pm 0.015 * 10^{-11} \text{ year}^{-1}$ based on the age comparisons of 4 samples from diverse localities and with different ages. This included two pegmatites from Norway with ages ~ 1.1 and 0.9 Ga, an apatite-xenotime bearing gneiss from New York State with an age of ~ 1.0 Ga, and a carbonatite from South Africa with an age of ~ 2.1 Ga. The U-Pb crystallization ages for these samples were based on the measurements of gadolinite, xenotime, baddeleyite, and apatite in these rocks; the Lu-Hf isochron was determined using the high Lu/Hf ratios of gadolinite, xenotime, and apatite combined with low Lu/Hf phases in the rock (baddeleyite, zircon, biotite) or the whole-rock compositions.

In a similar study, Söderlund et al. (2004) determined a $\lambda^{176}_{\text{Lu}}$ value of $1.867 \pm 0.008 * 10^{-11} \text{ year}^{-1}$ based on age comparisons using two Proterozoic dolerite dikes from Sweden. The ages of these rocks were determined using baddeleyite U-Pb geochronology; apatite was the high Lu/Hf phase providing the spread in the Lu-Hf isochron. Additional determinations by Scherer et al. (2003) agreed with the slightly faster decay of Söderlund et al.'s (2004) value. As a result of this agreement, the isotopic community is now using the $\lambda^{176}_{\text{Lu}}$ value of $1.867 \pm 0.008 * 10^{-11} \text{ year}^{-1}$. The half-life corresponding to this value is 37.12 Ga. The revision in the value for the ^{176}Lu decay constant from the Patchett (1983b) and Sguigna et al.'s (1982) values has two important consequences for Lu-Hf geochronology and isotope geochemistry. The first, and most obvious of these, is the change in calculated Lu-Hf ages. Using the Scherer/Söderlund decay constant results in ages that are 4 % older than ages determined with the Patchett/Sguigna value. The second consequence is that this lowers the calculated initial $^{176}\text{Hf}/^{177}\text{Hf}$ of rocks. The degree of this effect is a function of age but also of the $^{176}\text{Lu}/^{177}\text{Hf}$ ratios. For Archean and older samples, the lowering of the calculated initial $^{176}\text{Hf}/^{177}\text{Hf}$ for the Earth's oldest rocks has very significant implications for the record of the Hf isotope evolution of the Earth (e.g., Scherer et al. 2001, 2007).

Although the Söderlund/Scherer decay constant determinations, which used terrestrial samples in their age comparisons, have converged on a well constrained value of $1.867 \pm 0.008 * 10^{-11} \text{ year}^{-1}$, age comparison determinations based on meteorites continue to yield a faster ^{176}Lu decay rate. Blichert-Toft et al. (2002) reanalyzed a suite of basaltic and cumulate eucrites and concluded that their regression was consistent with the $1.93 \pm 0.03 * 10^{-11} \text{ year}^{-1}$ value of Sguigna et al. (1982) and not the slower decay rates determined from terrestrial age comparisons. As was true with the earlier work of Patchett and Tatsumoto (1980a), however, the basaltic and cumulate eucrites plot at opposite ends of the isochron with the basaltic eucrites at the low Lu-Hf end and the cumulate eucrites at the high Lu-Hf end, which may indicate these are not truly cogenetic. Further, these samples appear to have different formation ages with the cumulate eucrites arguably younger (Mittlefehldt et al. 1998). In another study using meteorite age comparison, Bizzarro et al. (2003) determined a $\lambda^{176}_{\text{Lu}}$ value of $1.983 \pm 0.033 * 10^{-11} \text{ year}^{-1}$, even faster than the Patchett/Sguigna values. The Bizzarro et al. (2003) study included analyses of ordinary chondrites, carbonaceous chondrites, and basaltic eucrites and used a common age of 4.56 Ga. As was true with the eucrite-based determination, this study included a diverse suite of meteorites of potentially different ages and metamorphic histories, and therefore, the decay constant determination may be affected in some way by the use of samples that do not strictly meet the requirements for an isochron. These caveats notwithstanding, there are indications that meteorite isochrons yield a faster decay constant. One possible explanation for this apparent difference between the terrestrial and meteorite determinations is the presence of excess ^{176}Hf in meteorites. This may have been produced by excitation of the long-lived radioactive isotope ^{176}Lu to a short-lived ^{176}Lu isomer early in the history of the solar

system that then decays quickly to ^{176}Hf , thereby producing the excess ^{176}Hf (Albarède et al. 2006; Thrane et al. 2010). The exact mechanism of how this might have occurred is still a matter of debate (Albarède et al. 2006; Thrane et al. 2010).

The Lu-Hf Isochron Method

All Lu-Hf geochronology uses the “isochron” method to determine absolute ages. Unlike some chronometers such as U-Pb in zircon where there is little, if any, daughter isotope at the time of mineral growth, in the Lu-Hf system, there is invariably an abundance of daughter isotopes present (i.e., “common Hf”). For this reason, it is not possible to determine the age of a single mineral sample by measuring the accumulation of daughter isotopes in the sample. Thus all Lu-Hf geochronometry relies on the isochron approach, which utilizes coexisting rocks and minerals to determine an age. Important assumptions in this approach include the following: (1) All the minerals formed at the same time (i.e., have the same age); (2) all samples are cogenetic (have the same isotopic composition at the time of formation); and (3) the sample being dated has been a closed system since the time of mineral growth.

The systematics of the Lu-Hf isochron method, using garnet geochronology as an example, is shown in Fig. 1: (1) Prior to mineral formation, whether in a magma or metamorphic protolith, the bulk rock has a low Lu/Hf ratio and (at least approximately) a uniform Hf isotopic composition at the hand sample scale. (2) During crystallization, or, in this example, metamorphism, different phases form with different Lu/Hf ratios, but all with the same initial $^{176}\text{Hf}/^{177}\text{Hf}$. (3) Over time, the Hf isotopic compositions of the different components evolve as a function of their Lu/Hf ratios with high Lu/Hf components evolving more quickly to elevated $^{176}\text{Hf}/^{177}\text{Hf}$ and low Lu/Hf components evolving more slowly. (4) At some later time, if the rock has been a closed system with respect to Lu and Hf, all components will have compositions that plot along a line that is a function of time.

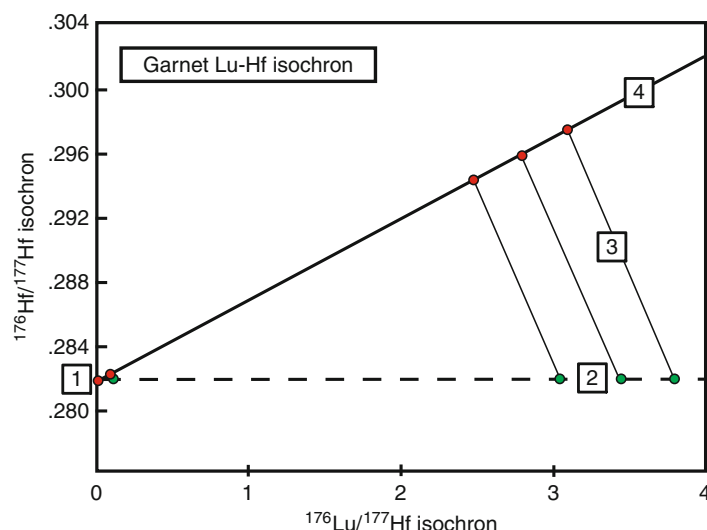


Fig. 1 The isochron method applied to garnet Lu-Hf geochronology. (1) uniform Hf isotopic composition at time $t = 0$; (2) phases in rock acquire different Lu/Hf ratios (garnets with high Lu/Hf), but all with the same $^{176}\text{Hf}/^{177}\text{Hf}$; (3) Hf isotopic compositions of the different components evolve with time as a function of their Lu/Hf ratios; (4) if the rock has remained a closed system with respect to Lu and Hf, all components will plot along a line (isochron) that is a function of time

Regression of a line through these points yields a slope from which an age can be calculated using the formula:

$$\text{Age} = \ln(\text{slope} + 1) / \lambda^{176}_{\text{Lu}}.$$

In detail, many of the assumptions of the garnet isochron method are not strictly met. In most cases the rock is certainly not in perfect isotopic equilibrium (i.e., homogeneous $^{176}\text{Hf}/^{177}\text{Hf}$) prior to metamorphism. In addition, the time different phases in the rock form may not be precisely the same, especially in the case of prolonged garnet growth (e.g., Kohn 2009). These can be serious obstacles if there is a small range of Lu/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ variations in samples but are often overcome in isochrons with high Lu/Hf phases and large amounts of radiogenic Hf ingrowth.

Geochronologic Applications

Whole-Rock Lu-Hf Isochrons

Because of the limited fractionation in Lu/Hf that occurs during magmatic processes, there is rarely a sufficiently large range in Lu/Hf ratios in suites of rocks that are truly cogenetic to generate an isochron with enough precision to be useful (Patchett 1983b). If there is a large variation in Lu/Hf in a suite of samples, it is likely these samples are probably not strictly cogenetic. Examples of the former may be represented by the eucrite isochrons combining both basaltic and cumulate eucrites (Blichert-Toft et al. 2002; Patchett 1983b) and in the collective chondrite-eucrite isochron of Bizzarro et al. (2003). In practice, therefore, Lu-Hf whole-rock isochrons are rarely employed for geochronology, especially for terrestrial samples.

Apatite Lu-Hf Geochronology

There is potential in some magmatic rocks, however, to crystallize a high Lu/Hf phase (e.g., apatite, magmatic garnet) that can then be used in geochronology. The magmatic rocks that have the most promise for useful geochronometry are those that contain apatite as a crystallizing phase. As demonstrated by the decay constant work of Scherer et al. (2001) and Söderlund et al. (2004) and the pioneering work applying Lu-Hf geochronology to phosphates by Barfod et al. (2003), apatite generally has very high Lu/Hf ratios and can be used in generating meaningful isochrons. In addition, these phases are likely in isotopic equilibrium with the magma at the time of their formation and likely formed at the same time as the other phases in the rock. Furthermore, apatite can occur in mafic rocks that generally lack zircon and that may not contain baddeleyite. The potential of Lu-Hf apatite geochronology for providing important geochronologic information for some rocks that are notoriously difficult to date is high, and this should be a growth area in the future.

Garnet Lu-Hf Geochronology

The most successful geochronologic application of the Lu-Hf system has been garnet geochronology. This technique shares the same principles as Sm-Nd garnet geochronology in that it utilizes garnet's generally high affinity for HREEs which results in elevated Sm/Nd ratios and (generally higher) Lu/Hf ratios in the garnets as they grow. The potential of the garnet Lu-Hf technique was first demonstrated by a number of papers in the late 1990s (Blichert-Toft et al. 1999; Duchene et al. 1997; Scherer et al. 1997). Following this early proof-of-concept work, there have been a large number of studies in a wide variety of metamorphic rocks: garnet-bearing pelitic schists, para- and orthogneisses, amphibolites, eclogites, and granulites (Anczkiewicz et al. 2004; Bird et al. 2013;

Cheng et al. 2008; Herwartz et al. 2011; Kelly et al. 2011; Scherer et al. 2000; Smit et al. 2013; Wells et al. 2012; Zirakparvar et al. 2010). Reliable garnet Lu-Hf ages have been reported for rocks as old as Archean (e.g., Smit et al. 2013) and as young as Miocene (e.g., Zirakparvar et al. 2011) and everything in between.

Although there are many parallels between Lu-Hf and Sm-Nd garnet geochronology, there are important differences between these two systems. *First*, the decay rate of the parent isotope in the Lu-Hf system, ^{176}Lu , is ~ 3 times faster than ^{147}Sm in the Sm-Nd system. This results in a higher rate of ingrowth in the radiogenic daughter, ^{176}Hf , compared to ^{143}Nd . *Second*, owing to the different geochemical behavior between a REE and a HFSE, there is generally more fractionation in the Lu/Hf ratios compared to Sm/Nd, which is especially manifest in phases like garnet and apatite.

Third, Lu is partitioned into garnet most strongly of all the REEs, while Hf is incorporated into garnet only weakly (Table 2). This often results in pronounced Lu-Hf zoning in the garnet with high Lu/Hf ratios in the core, due to the strong incorporation of Lu during early garnet growth, and with lower Lu/Hf ratios toward the rim due to the depletion of Lu in the garnet feeding zones. Because the very high Lu-Hf in the cores will exert a strong control on the slope of the regression, it has been suggested that Lu/Hf ages will be biased toward the early stages of garnet growth (Lapen et al. 2003; Skora et al. 2006). In this way, we would expect slightly older Lu-Hf garnet ages compared with Sm-Nd ages in a slowly growing garnet (Lapen et al. 2003; Skora et al. 2006).

Fourth, there are significant differences in the apparent closure temperature ranges in garnet between the two isotopic systems with garnets closing for Lu-Hf at a higher temperature than for the Sm-Nd system. Debate continues on closure temperature estimates of the Sm-Nd chronometer (e.g., Dutch and Hand 2009; Ganguly et al. 1998; Scherer et al. 2000; Smit et al. 2013; Van Orman et al. 2002), but appear to be in the range of ~ 700 – 750 °C for garnets 1 mm diameter and larger (Smit et al. 2013; Van Orman et al. 2002) and significantly higher (perhaps 100 °C or more) for Hf. This can lead to differences between the garnet Lu-Hf and Sm-Nd ages with the Lu-Hf ages

Table 2 Melt-solid partition coefficients for Lu and Hf in various minerals

Mineral	D(Lu)	D(Hf)	Melt	References
Olivine	0.0015	0.01	Basalt	McKenzie and O’Nions 1991
Clinopyroxene	0.233	0.28	Basalt	McKenzie and O’Nions 1991
Clinopyroxene	0.223	0.623	Basaltic	Hauri et al 1994
Clinopyroxene	0.256	0.433	Alk. basalt	Zack and Brumm 1998
Plagioclase	0.025	0.01	Basalt	McKenzie and O’Nions 1991
Orthopyroxene	0.22	0.06	Thol. basalt	Green et al 2000
Ilmenite	0.084	0.38	Alk. basalt	Zack and Brumm 1998
Rutile	0.0124	4.98	Tonalite	Foley et al 2000
Amphibole	2.1	0.54	Andesite	Bacon and Druitt 1988
Garnet	5.5	0.23	Basalt	McKenzie and O’Nions 1991
Garnet	7.1	0.24	Basalt	Johnson 1998
Garnet	57	0.57	Andesite	Hauri et al 1994
Garnet	23.5	3.3	Dacite	Irving and Frey 1978
Apatite	13.8	0.73	Andesite	Bacon and Druitt 1988
Apatite	21.5	0.878	Dacite	Fujimaki 1986
Zircon	196	958	Andesite	Fujimaki 1986
Zircon	689	971	Dacite	Fujimaki 1986

The partition coefficient, D, is defined as the ratio of the concentration of the element in the solid compared to melt. Values are from GERM database (<http://earthref.org/KDD/>) compiled from the original references listed above

systematically older (e.g., Scherer et al. 2000). In some granulite terranes that may have remained buried at mid- to lower-crustal levels for a prolonged time during and following garnet growth, these age differences can be large – as much as 50–70 m.y. (Smit et al. 2013; Vervoort et al. 2013). Experimental work also indicates significantly slower diffusion for Hf in garnets than the REEs (Ganguly et al. 2010), which collectively have similar diffusion rates. One possible consequence of the slower diffusion of Hf than Lu is that the garnet may effectively close to Hf diffusion before Lu, leading to changing Lu/Hf ratios, but static Hf isotopic compositions (Ganguly et al. 2010). This could potentially result in “isochron rotation” and garnet Lu-Hf ages that are artificially too old.

Finally, the presence of accessory phases (e.g., zircon, apatite, monazite, allanite), especially as inclusions in the garnets, presents a special challenge (e.g., Anczkiewicz and Thirlwall 2003; DeWolf et al. 1996; Prince et al. 2000; Scherer et al. 2000; Thoni 2002), and each of these minerals affects the Lu-Hf and Sm-Nd system in different ways. For the Lu-Hf system, zircons provide the biggest challenge. Zircons are extraordinarily enriched in Hf (~10,000 ppm Hf in zircon) relative to garnet ($\ll 1$ ppm) and, therefore, can easily overwhelm Hf concentration budget if present as inclusions in the garnets, thus lowering Lu/Hf ratios of the garnet dissolutions. Furthermore, inclusions of preexisting zircons, which are not likely to be re-equilibrated prior to metamorphic growth, can significantly lower the measured $^{176}\text{Hf}/^{177}\text{Hf}$ of the garnet sample since these zircons will have a less radiogenic Hf isotopic composition than the bulk rock. If these zircons are much older than the bulk rock, this difference can be significant. The incorporation of zircon Hf not in isotopic equilibrium with the protolith at the time of metamorphism in the analyses, either in garnet or as a dispersed accessory phase in the rock matrix, can result in erroneous ages (e.g., Scherer et al. 2000). Fortunately, what makes zircon resistant to isotopic equilibration during metamorphism also makes it resistant to dissolution, and thus zircon inclusions can be largely avoided with a nonaggressive dissolution protocol (e.g., Cheng et al. 2008; Lagos et al. 2007). Very high $^{176}\text{Lu}/^{177}\text{Hf}$ ratios (generally $\gg 1$) in the garnet analyses is an indication that zircon (very low $^{176}\text{Lu}/^{177}\text{Hf}$ ratios, usually 0.002 to 0.001) has not been significantly dissolved. Apatite inclusions (very high $^{176}\text{Lu}/^{177}\text{Hf}$ ratios) in the garnet can also potentially have an effect on an isochron if they either are not in isotopic equilibrium with the garnet at the time of metamorphic growth or are formed or closed to Lu-Hf diffusion at a different time than the garnet. The effect of apatite inclusions on garnet Lu-Hf geochronology, however, has not yet been examined in the literature. For the Sm-Nd isotope system, the inclusions that are most problematic are phases enriched in REEs and with low Sm/Nd ratios such as monazite and allanite. The effect of these inclusions is generally to drastically reduce the spread in the isochron. If present within the garnets and incorporated in the dissolution, the garnets will have low Sm/Nd ratios – often as low as the whole rock – thus eliminating the possibility of producing a meaningful isochron.

Lawsonite Lu-Hf Geochronology

A recent addition to the Lu-Hf geochronology toolbox is the use of the mineral lawsonite to date subduction zone processes (Mulcahy et al. 2009; Vitale Brovarone and Herwartz 2013). Depending on its paragenesis, lawsonite can have sufficiently elevated Lu/Hf ratios to produce meaningful isochrons. Lawsonite is an important index mineral formed during low temperature-high pressure subduction zone metamorphism and potentially provides one of the few tools we have available to date subduction zone processes. Initial work with this geochronologic tool has shown that when lawsonite forms on the retrograde path from the breakdown of garnet, it generally has elevated Lu/Hf

ratios and can yield robust Lu-Hf ages. When the lawsonite forms from the breakdown of zeolites on a prograde path, however, it may not develop elevated Lu/Hf ratios and, therefore, may not provide useful Lu-Hf ages (Mulcahy et al. in review). The full potential of this geochronologic tool is just now being explored.

Hf Radiogenic Isotope Geochemistry

As mentioned above, both Lu and Hf are lithophile and refractory elements with high condensation temperatures. Because of these characteristics, it has long been assumed that the abundance of these elements in the bulk Earth can be approximated by chondritic meteorites. It has also been long assumed that the isotopic composition of a refractory element such as Hf was homogeneous in the solar nebula and can also be approximated by chondritic meteorites. This is known as the Chondritic Uniform Reservoir model, or CHUR. Recent work, primarily based on the short-lived ^{146}Sm - ^{142}Nd isotopic system, has questioned whether the Earth is strictly chondritic in composition (see discussion in Sm-Nd section). Regardless of whether the Earth is strictly chondritic, the CHUR model provides an important reference value for a plausible bulk Earth composition. The Lu-Hf and Sm-Nd systems are used in tandem for planetary evolutionary studies for the important reason that these are the only two such isotopic systems in which all elements are lithophile and refractory.

The Bulk Silicate Earth and CHUR

Because of the analytical challenges in measuring Hf isotope compositions in Hf-poor (~ 0.10 ppm; McDonough and Sun 1995) chondrites accurately and precisely, the early Lu-Hf CHUR values had considerable uncertainty. There have been two approaches used to determine a CHUR value for the Lu-Hf and Sm-Nd isotope systems. For Sm-Nd, because there is very little fractionation between Sm and Nd in chondrites and there are no phases with low Sm/Nd ratios, it has not been possible to determine a chondritic (Solar System) initial value for this system. Instead, the approach has been to take an average of representative present-day $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ values of undifferentiated chondrites. This works because the total Sm-Nd variation in chondrites is modest. Using this approach, Jacobsen and Wasserburg (1980, 1984) determined present-day CHUR values of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1966$, which corresponded to the composition of two CI chondrites, Allende and Murchison.

The situation for the Lu-Hf isotope system was initially different because of the difficulty in measuring Hf precisely in the Hf-poor chondrites and the large apparent spread in $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ in chondrites, which makes determining a mean chondritic value more ambiguous. In order to compare this system to the more established Sm-Nd isotope system, Patchett and Tatsumoto (1981) based the Hf CHUR values on the same CI chondrites used to define the Sm-Nd isotope system, Allende and Murchison. Using this approach, they arrived at present-day values of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282860$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0334$. The $^{176}\text{Hf}/^{177}\text{Hf}$ value was later adjusted to 0.282830 (Vervoort and Patchett 1996) to account for the high $^{176}\text{Hf}/^{177}\text{Hf}$ bias on the TIMS in Denver, the instrument on which all the early pioneering Hf isotope work was performed.

With the advent of the MC-ICPMS and its application to measuring Hf isotopes came the ability to analyze Hf-poor chondrites more precisely. In order to constrain the Lu-Hf CHUR values, Blichert-Toft and Albarede (1997) analyzed 25 chondritic meteorites including carbonaceous, ordinary, and enstatite chondrites. Because the measured values of these samples had a wide spread in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ($\sim 18\%$) and did not define an isochron, they took the weighted average of the 25 chondrites to arrive at present-day values of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$.

The $^{176}\text{Hf}/^{177}\text{Hf}$ values were significantly lower by 0.000058 from the adjusted Patchett and Tatsumoto values (Vervoort and Patchett 1996).

In order to address the problem of the spread in Lu/Hf ratios and the scatter about a reference isochron, Bouvier et al. (2008) analyzed only unequilibrated chondrites (lower metamorphic grade, petrologic types 1–3) including 12 carbonaceous chondrites, 13 ordinary chondrites, and 3 enstatite chondrites. The resulting data had a much smaller spread in Lu/Hf ratios (only 3 %) which allowed a more precise determination of the present-day CHUR values: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785 \pm 11$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336 \pm 1$. These are the values currently in use by the geochemical and cosmochemical communities. Bouvier et al. (2008) also measured the Sm-Nd isotopic compositions of the same solutions on which the Lu-Hf values were determined and arrived at new CHUR values for the Sm-Nd isotope system of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1960$. Although these are very close to the values of Jacobsen and Wasserburg (1980, 1984), the Bouvier et al.'s (2008) values are more appropriate to use in studies reporting both Hf and Nd data relative to the chondritic reference because they represent values determined on the same set of chondrites.

As is true for the Sm-Nd system, Hf isotope data are often expressed in epsilon values, which are variations in parts per 10,000 from the CHUR reference. Expressed in terms of present-day compositions, this expression is:

$$\varepsilon_{\text{Hf}(0)} = \left[\left(^{176}\text{Hf}/^{177}\text{Hf}_{(\text{sample},0)} - ^{176}\text{Hf}/^{177}\text{Hf}_{(\text{chur},0)} \right) / \left(^{176}\text{Hf}/^{177}\text{Hf}_{(\text{chur},0)} \right) \right] \times 10^4.$$

Expressed in terms of compositions at any time in the past, t , this expression is:

$$\varepsilon_{\text{Hf}(t)} = \left[\left(^{176}\text{Hf}/^{177}\text{Hf}_{(\text{sample},t)} - ^{176}\text{Hf}/^{177}\text{Hf}_{(\text{chur},t)} \right) / \left(^{176}\text{Hf}/^{177}\text{Hf}_{(\text{chur},t)} \right) \right] \times 10^4.$$

Frequently, when values are calculated back in time, they are expressed as “initial” values, signifying the formation age of that rock or mineral. (It is important to note that the CHUR value also needs to be calculated back to its composition at time, t , from the present-day values.)

Lu-Hf Tracers of Geologic Processes

The current paradigm for the evolution of the Earth holds that the crust was formed from silicate melts extracted in some way from the mantle. The crustal rocks resulting from this process are enriched in incompatible elements (hence the term enriched crust), and the mantle left from this extraction of crust is depleted in incompatible elements (hence the term depleted mantle). As a consequence of this differentiation occurring throughout the history of the Earth, including at its very beginning, the Earth's different reservoirs have evolved following different paths. The crustal reservoirs are enriched in incompatible elements but have lower Lu/Hf and Sm/Nd ratios than bulk Earth, and so their $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ evolve more slowly. Conversely, the depleted mantle components, while depleted in incompatible elements, have higher Lu/Hf ratios and Sm/Nd ratios, and so their $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ compositions evolve more quickly than bulk Earth (Fig. 2a). In terms of epsilon values relative to bulk Earth (i.e., CHUR), depleted mantle components evolve toward positive epsilon values, and enriched crustal values evolve toward negative epsilon values (Fig. 2b). This is a fundamental feature in both the Hf and Nd isotopic records of Earth's evolution and has been used to great utility in a wide range of crust/mantle petrogenetic/geochemical studies.

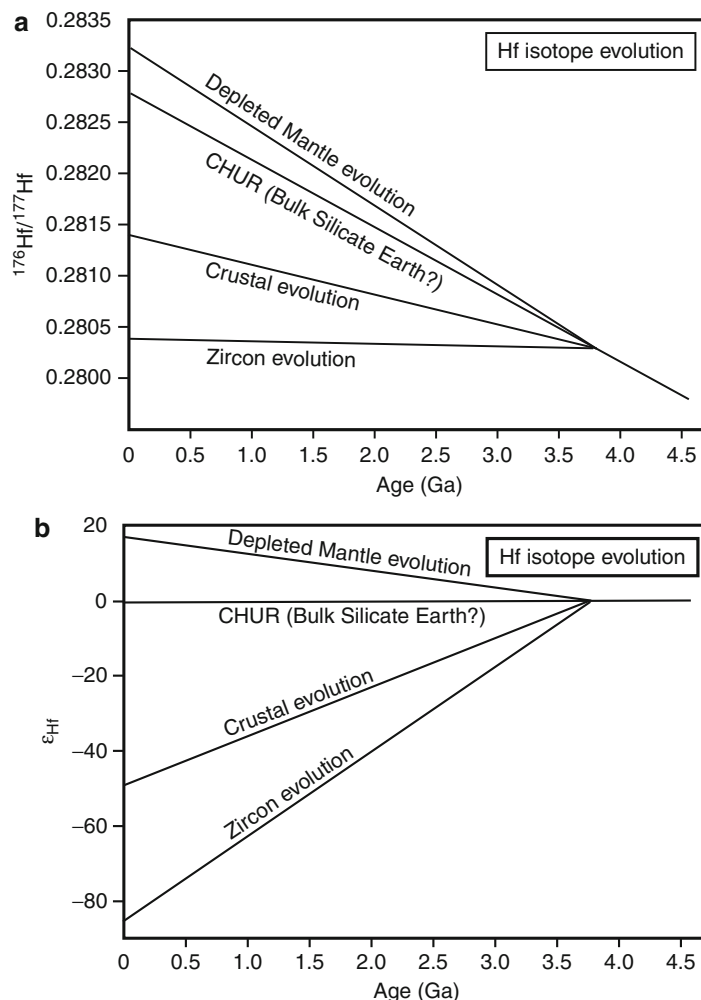


Fig. 2 Schematic diagram showing the hypothetical Hf isotope evolution of different terrestrial reservoirs following a major differentiation event at 3.8 Ga: Chondritic Uniform Reservoir (CHUR) broadly taken as representative of bulk silicate Earth (BSE), depleted mantle evolution from depletion at 3.8 Ga to its composition today, evolution of an enriched crustal reservoir ($^{176}\text{Lu}/^{177}\text{Hf} = 0.015$), and evolution of a typical zircon formed at 3.8 Ga ($^{176}\text{Lu}/^{177}\text{Hf} = 0.001$). (a) Evolution of $^{176}\text{Hf}/^{177}\text{Hf}$. (b) The same diagram in epsilon Hf notation

An important component in all radiogenic isotopes is time; time is an inherent aspect of Hf isotope evolution and therefore Hf isotope compositions can be used to qualitatively assess the time of separation from different reference reservoirs. These time estimates are called “model ages” and, although not ages in the strict sense, are still a useful way to represent and visualize data with a temporal framework.

The concept of a model age in the Lu-Hf isotope system follows that of Sm-Nd model ages (DePaolo 1981) and is illustrated in Fig. 3a. The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic composition of a sample is measured today, and the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of that sample is used to calculate its isotopic composition back in time until it intersects with a reservoir of interest such as the depleted mantle. The time, corresponding to this intersection, is a Hf model age – in this case, the Hf depleted mantle model age $\text{Hf}_{\text{T(DM)}}$. This model age has also been termed a crust-formation age, $\text{Hf}_{\text{T(CR)}}$, signifying the average time since separation from the depleted mantle or time of residence in a crustal reservoir (DePaolo 1981).

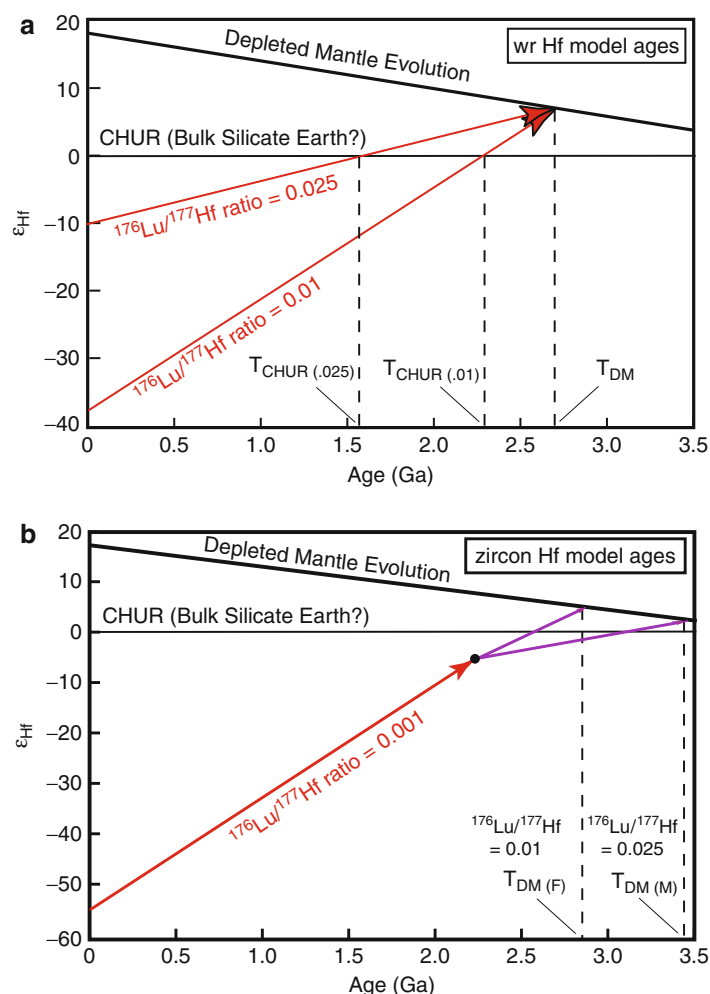


Fig. 3 (a) Schematic diagram showing the calculation of Hf model ages for two hypothetical whole-rock (wr) samples that formed from a depleted mantle reservoir at ~2.7 Ga: a mafic sample with a high Lu-Hf ratio ($^{176}\text{Lu}/^{177}\text{Hf} = 0.025$) and a negative present-day epsilon Hf value of approx. -10 and a felsic sample with a low Lu-Hf ratio ($^{176}\text{Lu}/^{177}\text{Hf} = 0.010$) and a highly negative present-day epsilon Hf value of ~-38. Also shown in this diagram are the depleted mantle model ages (T_{DM}) and the CHUR model ages (T_{CHUR}). Note the different trajectories for the two samples and the differences in T_{CHUR} . (b) Schematic diagram showing the calculation of zircon Hf model ages. In this example the zircon has a present-day epsilon Hf value of ~-55 and an initial epsilon Hf value of ~-5 calculated at a crystallization age of ~2.2 Ga. Calculation of depleted mantle model ages (T_{DM}) requires an assumption of the $^{176}\text{Lu}/^{177}\text{Hf}$ of the source rock. If the source rock is more evolved ($^{176}\text{Lu}/^{177}\text{Hf} = 0.01$ in this case), the T_{DM} is ~2.85 Ga. If the source rock is more mafic ($^{176}\text{Lu}/^{177}\text{Hf} = 0.025$ in this case), the T_{DM} is much older, ~3.45 Ga. As can be seen from this diagram, the uncertainty in the T_{DM} increases dramatically the further the initial Hf value is away from the depleted mantle reference line. Further, unrecognized Pb loss in the zircon, which would yield anomalously young crystallization ages, exacerbates the difference between crystallization and depleted mantle ages. See text for further discussion of zircon Hf model ages

Depleted mantle model ages have been used to identify the sources of magmatic rocks; if the Hf T_{DM} values are older than the crystallization ages, then the interpretation is that these rocks were derived from older sources or sources that had a crustal prehistory – sources that had separated from the mantle some time in the past. In this way it is simply another means of conveying the Hf isotopic compositions in the context of time – in much the same way as an epsilon Hf isotope diagram places the Hf isotope compositions in a time context. Model ages are also applied to sediments to identify

the provenance of their sources: more juvenile mantle-derived sources, older evolved crustal sources, or some mixture of the two. This is identical to the approach used for Sm-Nd model ages in sediments with the caveat that Hf model ages are often more variable than Nd model ages because of the presence or absence of Hf-rich (and unradiogenic) zircons in the sediments (e.g., Prytulak et al. 2006; Vervoort et al. 1999).

A recent adaptation of Hf model ages – and one that has seen an explosion of use in recent years – is the use of Hf model ages of zircons. The way this works is shown in Fig. 3b. The Hf isotopic composition is measured in the zircon and the zircon's Lu/Hf ratio is used to calculate back to its crystallization age. At that point, the growth trajectory changes, assuming a source $^{176}\text{Lu}/^{177}\text{Hf}$ ratio. As was the case with the other model ages, the intersection with the depleted mantle reference line yields the zircon Hf depleted mantle model age. This technique has recently been applied to detrital zircon studies because of the facility of acquiring U-Pb crystallization ages and Lu-Hf isotope compositions on the same zircon grain by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS).

There are several aspects of this approach, however, that result in considerable uncertainty in the zircon Hf model “ages.” Because the context of the rock has been lost, the Lu/Hf ratio of the zircon's precursor rock has to be estimated, and this value can vary widely from a mafic precursor (high Lu/Hf) to a felsic precursor (low Lu/Hf). The further the composition of a zircon is from the depleted mantle (or other) reference, the greater the uncertainty in the model age. Another limitation of this technique is that the model ages rely on the intersection of the zircon + precursor rock trajectory with a depleted mantle reference curve. The depleted mantle, however, is not a discrete entity with a discrete isotopic composition. It is, in fact, typically defined by its most depleted, rather than average, compositions (Vervoort and Blichert-Toft 1999). Finally, it is not possible to determine the true ages of some detrital zircons precisely, due to the potential for ancient Pb loss and other factors. If ancient Pb loss exists in these grains, this would greatly exacerbate the differences between the crystallization and the Hf model ages with the former being too young and the latter being too old. In total, all of these factors contribute to very large uncertainties in Hf model “ages.” It is tempting to treat these model ages, particularly for detrital zircons, as values with quantifiable age information rather than model-dependent estimates. It is important to recognize, however, that these model ages are not ages in any true sense of the word, but rather “models” with large uncertainties. While they provide some useful constraints on the timing and nature of crust forming events, it is imperative to understand the limitations of such “age” information.

Conclusions

The Lu-Hf isotope system is an important chronometer in geochemistry and cosmochemistry. Its utility as a chronometer in whole-rock samples, however, is limited by the relatively small degrees of Lu-Hf fractionation during magmatic processes. In rocks with high Lu-Hf phases, the Lu-Hf isotope system can be a powerful chronometer; this is especially true for garnet-bearing metamorphic rocks and magmatic rocks with apatite as a crystallizing phase.

There now appears to be widespread agreement on a value for the ^{176}Lu decay constant of $1.867 \pm 0.008 \times 10^{-11}$ Ga (Scherer et al. 2001; Söderlund et al. 2004). This value has important implications not only for Lu-Hf geochronology but also for early Earth differentiation and evolution based on calculated initial Hf isotope values. Similarly, there is currently widespread acceptance of the Bouvier et al. (2008) CHUR values of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$. Corresponding to these are the Sm-Nd CHUR values of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630$ and

$^{147}\text{Sm}/^{144}\text{Nd} = 0.1960$. Notwithstanding discussions of whether or not the Earth is strictly chondritic, these values provide a self-consistent baseline on which to reference the isotopic evolution of the Earth.

Tracer isotopic applications provide equal utility of the Lu-Hf isotopic system and, in conjunction with independent age information, can be used to determine the Hf isotopic composition of rocks and minerals back into time. This information is useful in constraining both the evolution and source regions of igneous systems as well as the provenance of sedimentary rocks. By far the most heavily utilized mineral for tracer isotope studies is zircon, which provides a unique opportunity for determining both age and Hf isotope compositions in individual crystals (and even separate growth zones within a single crystals), such as in the case of inheritance or overgrowths. For this reason, the integrated U-Pb and Hf isotope information from zircon has seen a rapid increase in use in recent years and will likely continue. Many of these studies often report zircon Hf model ages. While these provide useful qualitative, model-based data, these are not in any way truly ages and should not be interpreted as containing quantitative chronologic information.

In summary, with the full implementation of techniques and applications of the Lu-Hf isotope system following the advent of MC-ICPMS technology, Lu-Hf geochronology and tracer isotope work has finally taken its place at the table with the other main players in geochronology and radiogenic isotope geochemistry.

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Alpha Spectroscopy

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Synonyms

[Alpha counting](#); [Thick source alpha counting](#)

Definition

Measurement of U and Th concentrations in environmental samples through detection of alpha particles emitted by isotopes in the U and Th decay chains.

Alpha particles emitted during radioactive decay are extremely short range (in minerals, micrometers) but deposit a significant quantity of energy. Therefore, the isotopes responsible for alpha emissions may be a large contributor to the overall absorbed radiation dose for a datable sample.

In order to measure the U and Th concentrations in a mineral, the sample is ground to a powder and deposited on a scintillator screen (mounted to a photomultiplier tube) or on to a semiconductor detector. Alpha particles deposit significantly more energy than beta particles or gamma rays, so unwanted counts are rejected through electronic processing of the signals recorded by the detector.

Although thin samples would provide better energy resolution (essentially no loss of energy due to alpha particle interactions within the sample), thick samples are preferred in order to achieve acceptable count rates. The sample thickness is therefore greater than the maximum range of the naturally emitted alpha particles (“thick source alpha counting”). Alpha dose rates are determined from the count rate, sample density, and average alpha particle range of all alpha emissions in a given decay chain (Aitken [1985](#)).

U and Th concentrations may be determined through other techniques, such as instrumental neutron activation analysis (INAA) or x-ray fluorescence (XRF). However, thick source alpha counting and high-resolution gamma spectroscopy permit the identification of disequilibria in the U and/or Th decay chains (Michael et al. [2008](#); Sjostrand and Prescott [2002](#)). This can result in more accurate alpha dose rate measurements.

Cross-References

- ▶ [Electron Spin Resonance \(ESR\) Dating, General Principles](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Radiation Dose Rate](#)

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Band Structure

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Synonyms

[Electronic band structure](#)

Definition

Configuration of allowed and disallowed electron states. Crystals (structures consisting of regularly repeating units) typically have “energy bands” in which an electron may have any energy within a continuous, or nearly continuous, energy range. Energy bands are separated by “band gaps” which specify a range of energies which are impossible for an electron in that system to have.

A variety of models and mathematical tools can be used to determine the nature of a particular crystalline material’s electronic band structure from the basic principles of quantum mechanics. For discussion here, we will concern ourselves only with the highest-energy fully or partially occupied band (“valence band”) and lowest-energy unoccupied band (“conduction band”).

In an insulator, the ground state consists of a fully occupied valence band and an empty conduction band. The random excitations due to ambient temperatures are not sufficient to add enough energy to an electron so that it may occupy a state in the conduction band, where it is free to move. In contrast, the ground state of a metal consists of a partially occupied valence band. Here there is no energy gap, and even thermal excitations are sufficient to populate some higher-energy states in the valence, leaving behind unoccupied states of lower energy. Electrons may therefore absorb energy, be promoted to higher-energy states, move (conduct) through the crystal, and finally release energy when recombining with a so-called hole.

The physical basis of electron spin resonance, optically stimulated luminescence, and thermoluminescence dating (so-called “trapped charge” techniques) rely on defects in the otherwise perfect pattern of a crystal. These defects can introduce localized energy states in the band gap, and transitions between localized defect states and nonlocalized band states are responsible for the underlying physics of these techniques.

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Cross-References

- ▶ [Electron spin resonance \(ESR\) dating, general principles](#)
- ▶ [Luminescence Dating](#)
- ▶ [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)
- ▶ [Radiation Defect](#)

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Beta Counter

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Definitions

Beta counter: Instrument for the detection of beta particles and hence quantification of beta-emitting radioactive material.

Beta particle (b^-): Electron emitted from an atomic nucleus during a nuclear decay in which the atomic number (Z) increases by 1 (essentially, a proton is converted to a neutron with emission of an electron from the nucleus).

Proportional counter: A gas-filled radiation detector in which electrons are accelerated towards an anode, creating secondary ionization events in the gas, which in turn cause additional ionization events, etc. This cascade (Townsend avalanche; charge amplification) results in electronic pulses which are proportional to the energy originally deposited within the detector by ionizing radiation.

Liquid scintillation counter: A liquid-filled radiation detector in which a radioactive sample is dissolved into a liquid scintillator (typically based on an organic solvent such as toluene). Deposition of energy through ionizing radiation results in the emission of light by the liquid scintillator, with detection by one or more photomultiplier tubes.

Beta counters are used in “conventional” ^{14}C dating to measure the activity of ^{14}C . Regardless of detection technique, a measured count rate (decays/second [Bq] or equivalent) is related to quantity through the known half-life of ^{14}C .

Beta counting can also be used to directly measure environmental beta activity in luminescence dating dose rate determinations (Sanderson 1988; Roberts et al. 2003).

The relatively low energy of the beta particles emitted by ^{14}C requires attention to the detector counting efficiency. One approach is to convert the sample carbon to the gas CO_2 , which is mixed with a fill gas and introduced into a gas proportional counter. Alternately, the carbon can be converted to benzene and then mixed with a solvent and liquid scintillation cocktail for counting of light pulses emitted as a result of energy deposited by individual beta particles.

Cross-References

- ▶ [\$^{14}\text{C}\$ Dating](#)
- ▶ [Radiation and Radioactivity](#)

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Electron Spin Resonance Spectrometer

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Synonyms

Electron paramagnetic resonance spectrometer; EPR spectrometer; ESR spectrometer

Definition

Instrument for the detection of electron paramagnetic transitions, consisting of a tunable source of electromagnetic radiation, a resonant cavity, an electromagnet, and a detector.

The electron spin resonance (ESR) spectrometer is employed to detect electron paramagnetic resonance transitions. Although a wide variety of designs exist, the typical commercial continuous-wave spectrometer consists of (1) a microwave source tunable within a limited range of frequencies near 9.4 GHz; (2) a sample cavity, often cylindrical, capable of maintaining an electromagnetic standing wave; (3) an electromagnet capable of generating and ramping a uniform magnetic field, along with superimposed rapid oscillation up to 100 kHz in frequency; (4) a detection system which amplifies the reflected microwave signal; and (5) an internal magnetic field standard such as MnO.

Transitions between electronic energy levels may be induced by polarized electromagnetic radiation such that the energy of the incident radiation is equal to the difference in energy between the energy levels in question. In other words, the microwave source is used to generate a fixed energy (E) of incident radiation with frequency ν (where $E = h\nu$) which is reflected from the sample in the resonant cavity, and the energy reflected is recorded by the detector. The energy levels will vary with the strength of an external magnetic field. Therefore, “sweeping” the external magnetic field strength from low to high will allow for resonant transitions to occur at the appropriate combination of (fixed) microwave energy (frequency) and external magnetic field. Resonance involves a net absorption of incident energy, which is detected as a relative loss in reflected energy.

The faithful reproduction of any given resonant absorption signal requires careful attention to instrumental parameters, including (1) incident microwave power, (2) center field (magnetic field strength at the midpoint of the sweep), (3) scan width (range of the swept magnetic field), (4) modulation amplitude (amplitude of the superimposed 100 kHz oscillating magnetic field), (5) sweep time, (6) time constant (roughly, the characteristic time over which instrumental data is averaged), (7) number of sweeps, and (8) detector gain.

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Cross-References

- [Electron Spin Resonance \(ESR\) Dating, General Principles](#)

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Radiation Defect

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Definition

Radiation defects – These are divided into two types: (1) those produced by atomic displacements of normal lattice site elements during irradiation (intrinsic) which are later modified by ionizing radiation and (2) those created initially during growth of the crystal lattice by substitution of an impurity atom or molecule (extrinsic) that are later modified by ionizing radiation. These types of defects are radiation sensitive, that is, they accumulate with increasing levels of ionizing radiation.

Radiation defects are utilized in all forms of *trapped charge or radiation exposure dating*, i.e., thermoluminescence (TL), optically stimulated luminescence (OSL), electron spin resonance (ESR), and other less common techniques. Ionizing radiation from natural background sources creates ions and free electrons; these ions and/or electrons may be stabilized (trapped) as radiation-induced defects before recombination can occur at normal lattice sites. If a signal related to concentration of defects can be measured through a suitable technique (such as TL, OSL, or ESR) and if the signal can be related to the total absorbed radiation dose, then an age may be inferred from a measurement of signal intensity in combination with a determination of past radiation dose rate.

In many cases, the precise identity of the defect(s) responsible for a given dating signal may not be known.

One example of a known class of extrinsic radiation defects is the Al center. The parent center is an Al^{3+} ion substituting for Si^{4+} in quartz (crystalline SiO_2), accompanied by an interstitial cation M^+ for reasons of charge neutrality: $[\text{AlO}_4/\text{Li}^+]^0$, $[\text{AlO}_4/\text{Na}^+]^0$, and $[\text{AlO}_4/\text{H}^+]^0$ are neutral parent centers (Ikeya 1993). An electron released due to the action of ionizing radiation may result in a hole trapped at the Al defect site, with the cation diffusing away to form the stable radiation defect $[\text{AlO}_4/\text{h}]^0$. The concentration of Al defects may be determined through electron spin resonance spectroscopy at low temperatures (77 K).

An example of an intrinsic radiation defect is the E'_1 center in quartz. This is an oxygen vacancy charged with a single unpaired electron located on an adjacent silicon atom (Rudra and Fowler 1987).

Cross-References

- ▶ [Electron Spin Resonance \(ESR\) Dating, General Principles](#)
- ▶ [Feldspar Infrared Stimulated Luminescence](#)
- ▶ [Luminescence Dating](#)
- ▶ [Quartz](#)

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- [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)
- [Radiation Dose Rate](#)

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Gene Sequencing

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Gene sequencing is the process of determining the order of nucleotides (adenine, guanine, cytosine, and thymine) in a strand of DNA. The resulting DNA sequences can be analyzed using phylogenetic methods, molecular clocks, and other techniques.

In living cells, DNA is copied by the enzyme DNA polymerase. The two strands of the DNA double helix, which are complementary to each other, are separated and used as templates. New DNA strands are synthesized by the sequential addition of nucleotides complementary to each strand.

The sequence of nucleotides in DNA can provide useful information for various biological analyses. Over the past few decades, the traditional method of determining DNA sequences in the laboratory has been the Sanger chain-termination method. This was developed by Frederick Sanger and colleagues in the late 1970s (Sanger et al. 1977). The method uses modified versions of the four nucleotides that terminate the extension of the new DNA strand and that are labelled with a nucleotide-specific fluorescent marker. Using a mixture of modified and regular nucleotides, DNA synthesis proceeds until a modified base is incorporated into the new DNA strand by chance. Each strand will terminate at a different nucleotide along the gene sequence, depending on the progress of DNA synthesis. At the end of the reaction, fragments are separated according to length and a laser determines the fluorescence of each fragment. This produces a series of fluorescence peaks, allowing the nucleotide sequence to be determined. Sequences of up to 900 nucleotides can be produced in a single Sanger-sequencing reaction. To determine longer sequences of nucleotides, multiple reactions are required.

DNA sequencing has been transformed by the development of next-generation sequencing technologies, which parallelize the sequencing process on a massive scale. These methods allow entire genomes to be sequenced in a time- and cost-effective manner. In “amplified single molecule” sequencing – also termed “second-generation” sequencing – DNA is fragmented into short molecules, which are amplified and then sequenced in massively paralleled reactions. Several biotechnology companies have developed second-generation sequencing platforms, each using technologies for DNA amplification and sequencing (Margulies et al. 2005; Shendure et al. 2005; Bentley et al. 2008) (see also Mardis 2008; Quail et al. 2012). An ideal platform would maximize the number of sequencing reactions per run, be able to sequence long stretches of DNA, and have a very low error rate.

More recently, “true single molecule” (third-generation) sequencing methodologies have become viable (Clarke et al. 2009; Eid et al. 2009; Thompson and Steinmann 2010). These methods can detect fluorescence at the level of individual sequencing reactions, enabling DNA molecules to be sequenced directly without the need for amplification. These reactions are able to produce DNA sequences of several thousand nucleotides, in comparison to the much shorter fragments produced by second-generation sequencing.

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Luminescence Dating of Archaeological Sediments

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Definition

“Archaeological sediments” can be defined in two ways. First, it can refer to any sediment at archaeological sites even if the depositional agent is entirely geologic. A site is any locus where human activity, as identified by remains of that activity (artifacts), took place. The timing of that activity interests archaeologists. Dating sediments which contain or bracket artifacts is a proxy for dating the activity itself. Luminescence is a powerful tool for this because the event addressed is the deposition itself, assuming sunlight was sufficient to reset the signal during deposition or, if not fully, a well-bleached portion can be isolated. But luminescence is not dating the activity (Richter et al. 2009). Artifacts can be redeposited by geologic forces making their current location not where the activity occurred. To avoid misleading information, bridging arguments are required to link the event dated (last exposure to sunlight) to the activity of interest.

Secondly, “archaeological sediments” can refer to sediments who owe their deposition entirely or in part to human activity. Here the link between human activity and the dating event is direct, and bridging arguments are not required, as long as it can be shown that humans were indeed the depositional agent. The latter can be obscure if the human role is indirect, for example, when humans denude the environment of vegetation and become just a trigger for subsequent erosion.

Introduction

Luminescence dating has been applied to sediments in both cases (see earlier reviews by Roberts (1997), Feathers (2003), Jacobs and Roberts (2007)). In the former, the rationale is that the human activity cannot be dated with more precision in another way, either because the event of interest is outside the dating range of other methods, because the bridging arguments are less tenable than they are for luminescence, or because other suitable dating materials are not present. Luminescence becomes the method of choice only because other options are poorer. To be sure, the suitability of any method is not always known in advance, so many archaeologists recommend multiple methods on the premise that convergence in results lends more credibility to results because different bridging arguments are needed for each method. In the case of human-caused deposition, however, luminescence is the method of choice, because of its value as a direct dating method with no need for bridging arguments.

Where luminescence dating of sediments is a proxy for dating human activities, the contributions are largely substantive, with the only methodological (in terms of archaeology) issue related to bridging arguments. To argue that sediment dates are good proxies, the stratigraphy must have integrity with little postdepositional activity, and luminescence single-grain dating is uniquely

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suited to address this issue. On the other hand, where luminescence is applied to anthropogenic sediments, the contributions are methodological (e.g., how can earthen mounds be dated?), as well as substantive.

Africa and the Middle East

Most scholars agree that anatomically modern humans originated in sub-Saharan Africa and that Middle Stone Age (MSA) lithics represent their handiwork. However, a more contentious question is when did humans become cognitively modern and how and when did they colonize the rest of the world? Dating of complex stone industries called the Howiesons Poort and the Still Bay, which appear within the MSA in South Africa, was dated with this question in mind. Prior to luminescence applications, both industries remained poorly dated. Work by Jacobs and colleagues, who applied innovative single-grain dating to several sites, culminated in an argument (Jacobs et al. 2008) that Howiesons Poort dated 60–65 ka and Still Bay around 71 ka with a significant gap between them. Conversely, Tribolo et al. (2013), using single-grain OSL along with TL dating of burned lithics at Diepkloof, produced not only older dates but suggested the durations of both industries overlap and are substantially longer, as much as 50 ka. While this disagreement is bound to foster additional research, both groups have already made an important contribution. Prior dating was so coarse-grained that the best explanatory framework was correlation with environmental change. Now OSL provides dates of sufficient precision to decouple direct changes in lithics from direct changes in climate or other environmental variables. A precise chronology of the MSA is now possible, forcing archaeologists to build explanations that consider the selective role of the environment in a more complex fashion.

North Africa and the Middle East are also involved in this issue. The question in North Africa is the age of a complex lithic industry called Aterian, often cited as evidence of modernity. Traditional dating placed the Aterian no older than 40 ka, but luminescence has pushed back the age to more than 100 ka (Jacobs et al. 2012). This has muddled the issue, because industries attributed to modern human behavior in North Africa are as old and even older than those from South Africa, and both seem to have developed independently. How modern humans got from Africa to the Middle East centers on two routes: north along the Nile into the Levant and south across the Red Sea onto the Arabian Peninsula. Luminescence has contributed to this debate in two ways: by dating sediments relevant to climate change, because the routes were hospitable to travel only at certain times (e.g., Rosenberg et al. 2011), and by dating archaeological sites themselves (e.g., Armitage et al. 2011).

Asia

How modern humans dispersed across Asia is a question with few answers because the area is vast and the number of sites investigated are few, but luminescence has been applied here as well (e.g., Petraglia et al. 2007; Haslam et al. 2011; Demeter et al. 2012; Pei et al. 2010). In East Asia, thermally transferred OSL (TT-OSL) was introduced to achieve older dates on quartz (Kim et al. 2010). Perhaps the best-known luminescence dating in Asia has been applied to sediments containing remains of the small hominin, *Homo floresiensis*, in Indonesia. Despite the lack of a fast-bleaching component, TL using red emission helped determine a 18–38 ka duration for the relict archaic hominin, well into the time of modern humans (Morwood et al. 2004).

Australia

Two issues dominate the early prehistory of Australia: When did humans first arrive and were they responsible for the extinction of the Pleistocene megafauna (Roberts et al. 2001)? Prior to the

1990s, radiocarbon had established that humans were present in Australia by about 40 ka, but the application of luminescence dating produced dates of 60 ka or older (e.g., Roberts et al. 1998b). The work is critically reviewed by O'Connell and Allen (2004), who claim little evidence for arrival earlier than 45 ka. Postdepositional mixing is the issue. Single-grain dating measures an equivalent dose or "age" for each grain and can identify mixtures of different-aged grains, if other sources of variability, including heterogeneous dose rates, can be controlled (David et al. 2007). An early application overturned previous TL dating of more than 100 ka at Jinmium rock shelter in northern Australia, by showing that a portion of grains were poorly bleached (Roberts et al. 1998a). However, at one site, Malakunanja, with OSL ages in the 50–60 ka range, single-grain dating suggested no postdepositional disturbance (Roberts et al. 1998b). Understanding the demise of the megafauna depends on whether dating the extinctions coincides with dating human arrival, and luminescence has been used to argue for and against the correlation (Roberts et al. 2001; Price et al. 2011).

Europe

Modern humans spread into Europe 40–50 ka. Exactly when they arrived and how they replaced resident Neanderthals continue to generate a large literature, and luminescence has played a key role. The Bohunician lithic tradition in south-central Europe, dated by luminescence to about 48 ka, appears to be the oldest evidence for modernity (Hoffecker 2009). Richter et al. (2009) found the most reliable dates to be TL on lithics because of poor association for radiocarbon and bad postdepositional mixing for OSL. Among the oldest hominid sites in Europe, the Atapuerca karstic complex in northern Spain has been dated by luminescence. Berger et al. (2008) used TL and IRSL on potassium feldspars to produce stratigraphically consistent dates up to 960 ± 120 ka.

North and South America

Much of the modern human debate involves times beyond the reach of radiocarbon, but not so early settlement of the Americas. However, OSL is still being applied, not only as a supplemental dating method but more importantly to provide a direct measure of sediment mixing. The issue is whether people arrived prior to the appearance of the distinctive Clovis lithic tradition that spread across North America around 13 ka. Luminescence has been applied for several pre-Clovis claims (Feathers et al. 2006; Waters et al. 2009; Lahaye et al. 2013). The Debra L. Friedkin site in Texas (Waters et al. 2011) was dated by 49 closely spaced OSL dates on quartz-dominated fine grains, which remarkably are almost all in correct stratigraphic order. The pre-Clovis artifacts are dated 15–16 ka, but an anomaly is that the Clovis layer is dated about 14 ka and the succeeding Folsom layer at 13 ka, both older than their normal age range. Lubinski et al. (2013) applied single-grain and multigrain single aliquot IRSL dating at a mammoth site in Washington. With the bones was found a piece of flake debitage in colluvium dated 16 ka. Although most of the site has stratigraphic integrity, one sample showed an intrusion of 5 ka grains, raising the possibility that the flake is also intruded.

Dating Built Structures and Human Environmental Impact Using Associated Sediments

A continual problem in archaeology is obtaining dates for prehistoric structures, whether simple rock arrangements or monumental architecture. While often the artifacts associated with these structures are reasonably well dated, the structures themselves are not.

Earthen structures are sediments deposited by humans. Any stratum within these structures can presumably be dated to the time of deposition by OSL as long as the mode of construction insured well-bleaching. Our laboratory found fill to be poorly bleached in mounds in Louisiana, but soils underneath the mounds could be dated (Bush and Feathers 2003). The rationale is that soil (or any surface exposed for some length of time) will become partially bleached by turbation processes that bring grains to the surface. Single-grain analysis using minimum age models provides age estimates for when the soil was covered over and grains could no longer reach the surface.

The same principle of dating buried surfaces has been applied to rock structures, by dating sediment below the rocks (e.g., Rink and Bartoll 2005; Outram et al. 2010). In dating soils beneath rocks in anthropogenic rock patterns in Montana and Wyoming, the author demonstrated the zeroing effect of turbation by collecting samples vertically under the rocks. Five vertical segments were dated separately, and in all samples, the youngest grains were concentrated in the segment just below the buried surface (Feathers 2012).

For rock walls, Porat et al. (2012) recommended dating sediments trapped in between rocks as these are less likely to suffer postdepositional disturbance. Work has also been done dating mortar (Goedicke 2011; Feathers et al. 2008). Superimposed sediment over rock art has been dated by OSL (e.g., Yoshida et al. 2003; Mercier et al. 2012). Susino (2010) used OSL to date microlithic debitage, isolated using an SEM, to provide a direct date for knapping activity.

Dating prehistoric canals is challenging (Huckleberry et al. 2012; Sanderson et al. 2007). The event archaeologists want to know is the construction or use of canals. Fill deposited during use may be present, although distinguishing that from post-abandonment fill is difficult. Original construction sediments may also be preserved in berms, but the berms may also contain sediments from subsequent cleanouts. Poor bleaching may be the rule, as well as bioturbation that blurs boundaries. OSL has also been used to date other agricultural features including dams and terraces (e.g., Aiuvalasit et al. 2010; Beckers et al. 2013; Avni et al. 2012; Davidovich et al. 2012).

Luminescence methods have also helped understand the impact of human activities on the environment, most work with human-induced erosion (Fuchs and Lang 2009). Several studies have also used luminescence dating to reconstruct environmental context for archaeological remains, often to show how artifact distributions might be related to site formation studies (e.g., Rhodes et al. 2010).

Issues in Application of Luminescence Dating

Postdepositional mixing is a common problem in many archaeological sediments (Bateman et al. 2007). Single-grain dating is the solution, and despite difficulties in understanding single-grain distributions, it is still preferable to multigrain aliquots where averaging masks the problem. Work in understanding the extent to which sand grains move by various agents is just the beginning but vital (e.g., Tribolo et al. 2010). Several publications report ages for Paleo-Indian sites in Brazil, not to demonstrate pre-Clovis occupations but to show stratigraphic integrity. Two showed little postdepositional sediment mixing (Araujo et al. 2008; Feathers et al. 2010), including one with a skeleton dating 12–16 ka. However, two others did show mixing of sediment grains, although chronological information could still be obtained (Araujo et al. 2013; Bueno et al. 2013). Profiling, or making minimal measurements on several small samples, is also recommended to identify badly mixed samples (Burbidge et al. 2007), something that can now be done in the field by portable luminescence readers (Sanderson and Murphy 2010). Work is also being done to understand how postdepositional mixing can affect luminescence results by studying, for example, the movement of grains by burrowing insects (e.g., Rink et al. 2013).

Partial bleaching is an important issue in luminescence dating of archaeological sediments. Detection and accurate dating of partially bleached sediments remain an issue that is not fully resolved (e.g., Murray et al. 2012).

Many archaeologists think that quartz is best for dating and know little about dating with feldspars. The recent research emphasis on dating feldspars belies the old confidence in quartz. Quartz has two major problems. First, it saturates fairly early, making it problematic for dating older sediments. This might be an underlying factor in the debate over the dating at Diepkloof, discussed earlier, because the quartz there is near saturation. Second, quartz is relatively insensitive to luminescence on about half the planet, at least with commonly used UV emission. For older sediments and in areas where quartz is insensitive, feldspar becomes advantageous, despite the disadvantage of anomalous fading. Many strides in understanding the luminescence properties of and in dating feldspars have been made in the last 5 years (e.g., Lamothe et al. 2012; Jain and Ankjærgaard 2011), particularly in the use of high-temperature stimulations. High-precision feldspar dating should be a major goal for dating archaeological sediments. In areas where even the feldspars are insensitive, more research into red TL is needed (Westaway 2009).

Conclusions

In the last decade, application of luminescence dating to archaeological sediments has increased in quantity, variety, and innovativeness. Large portions of the pre-40 ka archaeological record, particularly in Africa, are now much better known. Luminescence dating has allowed archaeologists to greatly expand their knowledge on the age of built structures. Luminescence has increased information on how humans have impacted the environment and how the environment has affected humans. It has become a major tool in site formation studies and establishing an environmental context. Single-grain dating has become a tool to investigate stratigraphic integrity and bioturbation.

Cross-References

- ▶ [Luminescence Dating](#)
- ▶ [Luminescence, Coastal Sediments](#)
- ▶ [Luminescence, Colluvial Sediments](#)
- ▶ [Luminescence, Dispersion of Early Humans](#)
- ▶ [Luminescence, Fluvial Sediments](#)
- ▶ [Luminescence, Geomorphic Processes](#)
- ▶ [Luminescence, Single-Grain Age Distributions](#)
- ▶ [Luminescence, Soils](#)

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Historical Development (of Dating Methods)

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Synonyms

[Absolute dating](#); [Isotopic dating](#); [Isotopic geochronology](#); [Radio-isotope dating](#); [Radiometric dating](#)

Definition

H. S. Williams (1893) originally proposed the term “geochronology” for the study of the time scale of geological events. Williams coined the term just 3 years prior to the discovery of radioactivity, at a time when science-based estimates for the age of the Earth and the age of major geologic events were derived from various physical and chemical models, and a range of geologic observations and measurements. The discovery of radioactivity in 1896 by the French physicist, Henri Becquerel, led to the development of dating methods primarily based on the decay of long-lived, naturally occurring radioactive “parent isotopes” to stable “daughter isotopes.” In modern usage, “geochronology” is used more or less exclusively to refer to dating geological materials using methods based on radioactive decay.

Introduction

To quote Frank Richter’s paper on “Kelvin and the age of the Earth” (1986, p. 395): “The true vastness of geologic time, and the overthrow of the Biblical chronology that would measure it in generations of man, is in my view the most profound of geology’s many contributions.” In fact, the problem of determining the age of the Earth is also an ideal framework for a discussion of the history of geochronology. And the discussion is a lively one, replete with religious repression; battles among the titans of physics, biology, and geology; the dawn of a new scientific age with the discovery of radioactivity; and finally, the emergence of modern geochronology based on radioactive decay systems. This contribution will begin with a brief discussion of the influence of theological chronologies for the age of the Earth, followed by the gradual emergence of science-based models for the origin, nature, and age of the Earth and solar system in the face of religious persecution and, later, less lethal religious disapproval. Next is a discussion of the great scientific battles on the age of the Earth from the mid-1800s into the early 1900s that pitted leading physicists such as Lord Kelvin against the leading geologists of his day, and also against Charles Darwin and his theory of origin of the species and natural selection. Interesting subplots involve George Darwin (second son of Charles Darwin) and also John Perry (former protégé of, and assistant to Kelvin).

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Then came the scientific revolution that began with the discovery of radioactivity by Henri Becquerel in 1896, revolutionizing physics and giving birth to geochronology in its modern sense. Finally, over the past 100 years or so, “modern” geochronology has developed and matured into an essential field for the study of Earth, moon, and solar system origin and history.

Each section includes specific references within the text as needed, and a list of more general references at the end of the section.

Age of the Earth from Religious Sources

Many ancient civilizations developed creation stories, some including specific ideas about time. The ancient Greeks, Hindus, Chaldeans, and Mayans believed in infinite time, usually in the form of repeated cycles, each one lasting millions of years. The longest cycle in the Mayan “long count” calendar lasted ca. 6.3×10^7 year. However, far more important in the western world over the past 2,000 years or so were numerous calculations for the date of creation of the Earth and humans, using as a starting point Biblical sources such as the Book of Genesis. Beginning in about 169 A.D., church scholars calculated a series of very young ages for the Earth ranging from ca. 6,000 to 9,000 years BP.

James Ussher (1581–1656), an Archbishop in the Irish Anglican Church, published the most influential “age of the Earth” in the 1650s. Ussher’s date of October 22, 4004 B.C. for the creation of the Earth was not the first ca. 4000 B.C. calculation, but it was inserted as a marginal note into the 1701 edition of the English Bible, some 45 years after Ussher’s death. Insertion into the Bible, even as a marginal note, gave the 4004 B.C. date all the weight of inerrant Biblical truth to those who believed in a literal, word for word interpretation of the Bible. This had a profound impact on the emergence of scientific inquiry. Long before Ussher’s date was embedded in the Bible, holding, teaching, and/or publishing views that conflicted in any way with church dogma could lead to charges of heresy. However, the threat of persecution fluctuated, depending whether the Roman Catholic Church had more serious issues to deal with at any given time. For example, Copernicus (1473–1543) published his book on the heliocentric theory of the solar system in 1543. He actually dedicated the book to the sitting Pope, even though the heliocentric model was obviously in direct conflict with the geocentric solar system/universe of Genesis. However, at the time, the Roman Catholic Church had other, more pressing issues to deal with.

The “Protestant Reformation” of Martin Luther began in ca. 1517 with the printing and posting of Luther’s “disputations.” The movement spread rapidly, and grew into a more and more serious threat to the Roman Catholic Church. In the 1530s, Henry VIII implemented the “English Reformation” and also broke away from the Roman Catholic Church. Little wonder then that Copernican theory was a relatively low priority for Church investigation. As a result, the work of Copernicus, and those who supported his work, such as Galileo, escaped formal condemnation for many decades. By ca. 1545, only 2 years after the death of Copernicus, the Catholic Church began a formal “Counter Reformation.” However, when reformation movements continued to grow, even spreading into Italy, the Roman Catholic Church took a more extreme step, instituting a new inquisition, the “Roman Inquisition,” in 1588. In the early years of the inquisition, heliocentrism was still not the highest priority, but in 1616 the Church finally got around to Copernicus (73 years after his death!) formally denouncing the heliocentric model of Copernicus as “dangerous to faith” and banning his book.

At the time of the denunciation and ban, Galileo already had been publishing material in support of Copernicus for several years, based in part on his own telescopic observations. Galileo was

required to appear before a powerful Cardinal who ordered him not to “hold or defend” Copernican theory. Presumably, Galileo complied with this order for several years. However, in 1623, an old friend of Galileo’s became Pope Urban VIII, and Galileo was emboldened to publish about Copernican theory in a way that he thought might not directly violate the Cardinal’s orders. In 1632, Galileo published a book on Copernican theory, thinly disguised as a conversation between fictional characters, one arguing for, and the other against Copernican theory. One character, “Salviati” (obviously Galileo), brilliantly presented evidence supporting Copernican theory, including detailed astronomical observations, graphs, etc. The other character, the unfortunately named “Simplicio” (representing the Church, perhaps even the Pope himself), comes across as dim-witted, befuddled by Salviati’s arguments, and able only to present the standard church position in opposition to Copernican theory. The one-sided nature of the “debate” was all too obvious. Galileo was examined by the inquisition, found guilty, forced to recant, his book was banned, and he was placed under house arrest for the rest of his life. It took just over 200 years for Galileo’s book to be removed from the banned book list. Little wonder then, that for many years, most observers of the natural world carefully fitted their interpretations into the time frame of Archbishop Ussher, either from true belief or self-preservation. To quote Burchfield (1990, p. 5): “The question to be answered by the natural philosopher was not how long it had taken for geological forces to sculpture the face of the Earth, but how they had accomplished their work in the few millennia since Creation.”

General references (listed alphabetically): Albritton (1980), Burchfield (1990), Dalrymple (1991), Holmes (1913), Stanford Encyclopedia of Philosophy (<http://plato.stanford.edu/entries/copernicus>), Stanford Encyclopedia of Philosophy (<http://plato.stanford.edu/entries/galileo>).

Age of the Earth from Early Scientific Methods: Pre-Kelvin

Eventually, scientists began to push more openly against the constraints placed on them by an Earth only several thousand years old. As the science of geology began to emerge, in particular, the study of processes such as uplift, erosion, and sedimentation, the concept of a far more ancient Earth began to emerge. Initially, caution was still required. For example, Benoit de Maillet (1656–1738), French diplomat and naturalist, traveled widely as a diplomat and made many observations of geology and geography around the Mediterranean. He concluded that the Earth must be greatly older than the Ussher Biblical chronology suggested, perhaps on the order of 2 Ga. He presented his theory, based on a theory of steady gradual lowering of sea level over geologic time, in the form of fictional conversations between a French missionary and an Indian sage named “Telliamed” (de Maillet spelled backward). Having been born only 14 years after the death of Galileo, de Maillet would have been well aware of Galileo’s persecution, so he took the additional precaution of arranging for his own book to be published in 1748, 10 years after his own death.

One of the most remarkable scientific figures of the eighteenth century was Georges-Louis Leclerc (1707–1788), later the “compte de Buffon,” courtesy of King Louis XV of France. In 1749, just 1 year after the posthumous publication of de Maillet’s theory, Buffon published the first 3 of his 35 volumes on “Natural History...” Buffon, who would become one of the giants of the Enlightenment, proposed a detailed theory for the origin of the planets that was clearly at odds with Genesis. However, he claimed that his theory was only “pure philosophical speculation.” This, plus the fact that Buffon had the strong support and protection of Louis XV, saved him from any serious action by the Church. Of even more interest from the perspective of geochronology are the scientific experiments Buffon conducted to provide some actual numerical estimates of the age

of the Earth. In addition to his many other talents and enterprises, Buffon owned an iron foundry. On the theory that the Earth had cooled from an originally molten state, Buffon had his workers make a series of spheres of graduated sizes, some of pure iron, others mixtures of iron and silicates. He had the spheres heated to just below the melting point, then measured the time required for the surface of each sphere to cool to the point where it could be touched with a bare hand without burning the fingers, then the time for the surface to reach room temperature. From these data, Buffon extrapolated how long it would take for a sphere the size of the Earth to cool. The “short version” of the results, published in 1778, gave a result of 75 Ka for the Earth to cool to its present temperature. “Long chronologies” found in Buffon’s unpublished manuscripts give results as high as 3 Ma. Why the large discrepancy? “Internal evidence strongly suggests that Buffon favored the longer version. Why, then, did he elect to publish the shorter? . . . The best guess is that he thought the lower figure was about as much as the traffic would bear.” (Albritton 1980, pp. 85–86).

With the emergence of “the Enlightenment,” and especially in non-Catholic countries, it became more acceptable to challenge the Biblical chronologies. For example, James Hutton (1726–1797) published a paper in 1785 that would revolutionize geologic thinking. Hutton’s studies convinced him that ordinary geologic processes acting over vast amounts of time could explain all of his observations. Hutton saw no need for great Biblical catastrophes, such as Noah’s flood. Working in Scotland, Hutton did not have to fear an inquisition, but religious beliefs were still strongly held by many. To paraphrase one of Hutton’s most caustic critics: “. . . the suspicion of the high antiquity of the globe has been fatal to Mosaic (i.e., Biblical) history, and consequently to religion and morality” (see Burchfield 1990, p. 7, emphasis added). Charles Lyell (1797–1875) published his *Principles of Geology* in 1830, reinforcing and popularizing Hutton’s concept of gradual changes over “inconceivably vast” periods of time. Charles Darwin (1809–1882), a contemporary, friend, and admirer of Lyell, published *On the Origin of Species* in 1859, depending heavily on the availability of great expanses of time for the operation of natural selection.

General references: Albritton (1980), Burchfield (1990), Dalrymple (1991), Holmes (1913).

Age of the Earth from Early Scientific Methods: The Kelvin Era

The writings of Hutton, Lyell, and, in particular, *On the Origin of Species* by Darwin served as a major catalyst for a great flowering of inventive approaches for estimating the age of the Earth (or the oceans, or the sun, or the moon, or the Earth “as an abode fitted for life”) from the mid-1800s to the early 1900s. Scientists applied physics, chemistry, and geology to the “age of the Earth problem.” The age estimates based on a wide range of approaches varied over orders of magnitude and sparked several decades of heated and sometimes bitter controversy. The central figure was William Thomson (1824–1907), later known as Lord Kelvin, courtesy of Queen Victoria’s 1892 elevation of Thomson to a “peer of the realm.”

Kelvin was widely regarded as the most brilliant physicist of his era by his peers. Kelvin evidently strongly agreed with this opinion, and he was particularly resistant to changing any of his ideas, even in the face of new information, which he did not always keep up with anyway: “Kelvin’s failure to keep up with the literature even in his own field was notorious. It led him frequently to repeat experiments and discoveries already in the literature” (Burchfield 1990, p. 54). As with many other scientists of his era, Kelvin had broad interests, including geology, but geology’s lack of quantitative rigor annoyed him. He particularly objected to “uniformitarianism,” as proposed by Hutton and expanded by Lyell. The idea of terrestrial conditions such as surface temperatures remaining largely the same over unimaginably long periods of Earth history was

anathema to Kelvin. After all, Kelvin had discovered the second law of thermodynamics. The Earth had to be cooling, with a consequent slowing down of geologic processes over time. Kelvin was also annoyed by Charles Darwin's demands for vast lengths of time for the process of natural selection. Starting in ca. 1862, and extending for over the 40 or so years, Kelvin fought a running battle with geologists, biologists, and even fellow physicists. Starting in the 1860s, Kelvin published a series of papers on the age and energy source of the sun, the age and thermal history of the Earth, and the effects of tidal friction retarding the rate of rotation of the Earth. All of these studies were designed to place quantitative limits on the age of the Earth as a planet, or "the age of the Earth as an abode fitted for life."

Kelvin's work on the thermal history of the Earth is perhaps the best known. His approach was similar to that of Buffon, except that Kelvin used data from the Earth itself, rather than from experiments on small spheres. Kelvin assumed that the Earth initially was totally molten, solidified completely from the core outward, then cooled entirely by conduction to its present thermal state. He used measured thermal gradients from wells and mines, measured thermal conductivities for a few common crustal rock types (and assumed that these conductivities applied to the entire interior of the Earth), and then applied the mathematical approach to heat transfer published by Fourier in 1822. Kelvin derived an "age" for the Earth (at least, the time since the outermost crust solidified) of 98 Ma, but allowed a range of 20–400 Ma, based on uncertainties of his data. The ca. 100 Ma figure published by Kelvin in 1862 is widely quoted, but over the following decades, Kelvin reduced both his estimate for the Earth's age, and the uncertainties. To quote Burchfield (1990, p. 43):

By 1868 he was convinced that sufficient evidence existed to justify limiting the assumed duration of life on Earth, if not the Earth's total age, to no more than 100 million years. In 1876, he was willing to accept an upper limit of only 50 million years for the Earth's age, and in 1881 a limit of 20 to 50 million years. Finally, in 1897, he declared that the Earth's age was nearer 20 million than 40 million years, and embraced Clarence King's estimate of 24 million years as the best available.

Also in 1862, Kelvin published estimated age limits of 10–500 Ma for the sun – quite similar to his original limits for the age of the Earth of 20–400 Ma. Kelvin ruled out chemical reactions as a source of energy for the sun and proposed that the sun's heat had been produced primarily by gravitational accretion during its formation. Thus, he viewed the sun, like the Earth, as a simple cooling body with no internal source of energy. As Kelvin's estimates for the age of the Earth came down, he eagerly accepted younger estimates of the sun's age published by some of his colleagues. As the assumptions of his original work on the age of the Earth came under attack, he relied more heavily on these estimates of the sun's age to cling to his original conclusions about the Earth.

One of the more fascinating approaches by Kelvin was based on retardation of the Earth's rotation by oceanic tidal friction and the implications for the Earth's equatorial bulge. Kelvin pointed out that a totally molten Earth would assume a polar flattening and equatorial bulge in proportion to its rate of rotation. Kelvin then assumed that when the Earth completely solidified, it would become many times more rigid than steel and could no longer respond to changes in the rate of rotation. Thus, Kelvin reasoned, the equatorial bulge would be locked in at the time of solidification. By knowing the rate of slowing of the Earth's rotation, one could theoretically calculate when, in the past, the rate of rotation matched the supposedly locked in (present) shape of the Earth. In fact, the present shape of the Earth is consistent with its present rate of rotation. Kelvin, recognizing that there were great uncertainties in his approach, concluded that the data could only limit the age of the Earth's solidification to <1 Ga. What he failed to recognize (or chose to ignore) was that a "young" Earth was not the only explanation for the agreement between the present shape of the Earth and the present rate of rotation. The data were also consistent with the

present-day Earth being nonrigid – capable of flowage and continuously adapting its shape to the slowing rotation rate of the Earth.

One of the interesting “subplots” in the “age of the Earth” debate was the involvement of George Darwin, the second son of Charles Darwin. George Darwin, an eminent and respected scientist in his own right, was a professor of “astronomy and experimental philosophy” at Cambridge for almost 30 years. Early in his career, he had attracted the attention of Kelvin, who responded enthusiastically to George’s first major paper on the effects of geological change on the Earth’s rotation. Kelvin encouraged George to analyze the tidal interactions of the Earth-moon system, to follow up Kelvin’s Earth-ocean tide study. The work led to George’s well-known 1879 theory that the moon had spun off from the Earth during an earlier era of more rapid rotation. The calculations also gave a *minimum* age of 54–57 Ma for the Earth/moon system to reach the present Earth/moon axial rotation rate/orbital period, but Darwin pointed out that the *maximum* age might be very much greater. As might be expected, Darwin’s theory of lunar origin sparked considerable interest by both the scientific community and the general public. Unfortunately, popular versions tended to be oversimplified: “Thus too little emphasis was given to the fact that the figures 54 million and 57 million years for the moon represented possible minima and in no way limited the maximum age of the Earth-moon system. Instead these figures passed into the literature as still another proof that the Earth *must* be less than 100 million years old” (Burchfield 1990, p. 115). It is interesting that George Darwin’s calculations were all based on a viscous, nonrigid Earth. This stands in sharp contrast to Kelvin who based both his cooling and tidal models on a completely rigid Earth. Instead, Darwin’s model of a viscous Earth was in accord with geological data that were being used at about the same time to attack Kelvin’s age(s) for the Earth.

General references: Albritton (1980), Burchfield (1990), Dalrymple (1991), Holmes (1913).

Age of the Earth from Early Scientific Methods: The Geologists Fight Back

Some geologists (and a few physicists) began attacking Kelvin’s assumptions. No one was willing to challenge Kelvin’s prowess as a mathematician, but many believed that Kelvin’s assumption of a rigid Earth, physically uniform throughout, was the Achilles heel of his model. For example, the Reverend Osmond Fisher (1817–1914), an early geophysicist from the long and rich tradition of theologically trained naturalists, mounted an attack against Kelvin. In “Physics of the Earth’s Crust,” published in 1881, Fisher summarized evidence for depression of the Earth’s crust in Scandinavia by glacial ice-loading and post-glacial rebound of the crust after the glaciers had melted. It was obvious to Fisher that the geological evidence was completely incompatible with Kelvin’s rigid Earth assumption, instead requiring the crust to float on a viscous interior. Fisher continued his attacks in a series of papers with titles such as “On depression of ice-loaded lands,” published in 1882, and “Rigidity not to be relied on in estimating the Earth’s age,” published in 1893.

Even more telling were the analyses of John Perry (1850–1920). Perry was a brilliant mathematician and also a former student, assistant, and collaborator of Kelvin’s. Perry was obviously fond of Kelvin and thus was reluctant to criticize Kelvin’s work on the age of the Earth, making this another interesting “subplot” in the controversy over age of the Earth: “Some of my friends have blamed me severely for not publishing the above document sooner. I was Lord Kelvin’s pupil, and am still his affectionate pupil. . . . He has been uniformly kind to me, and there have been times when he must have found this difficult” (Perry 1895). Affection and respect notwithstanding, Perry was particularly concerned with Kelvin’s simplistic assumptions that the Earth’s physical

properties, including thermal conductivity, were uniform throughout and that the Earth was rigid, with no possibility for convection. Suppose “quasi-conductivity” (conduction plus some convection) allowed the transfer of heat from the Earth’s interior to the base of the crust at ten times the rate based on Kelvin’s measurements of conductivity of typical upper crustal rocks? Perry (1895) demonstrated that such an increase in heat transfer from the Earth’s deep interior would increase Kelvin’s calculated age for the Earth by a factor of 56. Perry’s goal was not to calculate a specific age for the Earth but to show that Kelvin greatly underestimated his *upper limit* for the age of the Earth. Perry (1895, p. 227) includes a letter from Kelvin, in which Kelvin more or less concedes this point: “. . . I thought my range from 20 millions to 400 millions was probably wide enough, but it is quite possible that I should have put the superior limit a good deal higher, perhaps 4000 instead of 400. . . .” However, Kelvin quickly reverted to much younger age limits. Even after the discovery of radioactivity, the production of heat from radioactive decay, and publications of the first dates based on radioactive decay, Kelvin clung tenaciously to his earlier ideas.

Meanwhile, geologists had devised methods of their own to calculate the age of the Earth. Particularly popular were methods based on observed thicknesses of sedimentary rock coupled with estimated rates of erosion and sedimentation and methods based on ocean chemistry, predominantly those based on sodium accumulation. Excellent, detailed, and very readable accounts have been provided by Albritton (1980), Burchfield (1990), and Dalrymple (1991) and are very briefly noted here. Between 1860 and 1917, some 32 papers by 21 different authors estimated the ages of various parts of the sedimentary record, based on erosion and sedimentation rates (Dalrymple 1991, Table 2.1). Results varied wildly from ca. 3 Ma to ca. 15 Ga, but some efforts were remarkably accurate. For example, John Goodchild in 1897 published a detailed analysis of the Phanerozoic sedimentary record. To quote Burchfield (1990, p. 148): “Goodchild’s approach was eclectic. Borrowing freely from the methods pioneered by Phillips, Reade, Geike, and others, he determined the duration of each separate geological period using what he regarded as the most appropriate and reliable method for each. . . . In all, he determined the ages of 15 geological periods since the beginning of the Cambrian, totaling just over 700 million years. . . .” This is a stunning result, considering that our present age for the beginning of the Cambrian is just over 540 Ma, less than 25 % below Goodchild’s figure. Goodchild also estimated “at least an equal duration for the Precambrian” for an age of the Earth >1.4 Ga. However, a significant number of the other estimates based on sedimentation and erosion did fall within Kelvin’s original 20–400 Ma age limits.

Between 1876 and 1931, some 12 papers by nine different authors used the chemistry of the oceans to place limits on the age of the Earth (Dalrymple 1991, Table 2.1). Most of the studies used methods based on sodium in the oceans. Perhaps the best-known results and those most widely quoted in elementary texts were by John Joly (1857–1933). In 1899, Joly proposed a simple model: (1) that the primordial oceans were freshwater, condensed from the Earth’s atmosphere when surface temperatures dropped below the boiling point of water soon after the Earth’s crust solidified, and (2) that over the remainder of the Earth’s history, the oceans gradually became more and more salty by the addition of sodium weathered from the continents and carried into the ocean by rivers. The concentration of Na in the oceans was already well known, the volume of the oceans had been estimated, and the Na contents and discharge rates of most major rivers were approximately known. Joly had only to divide the total Na in the oceans by the annual Na flux of the rivers to estimate the age of the oceans, and the time elapsed since the Earth had cooled below the boiling point of water. Applying a few corrections and allowing for uncertainties in the data, Joly calculated that the oceans had an age between 80 and 90 Ma. In 1900, Joly adjusted his estimate slightly upward, to 90–100 Ma. Comparable calculations by other authors using slightly different

inputs arrived at more or less identical results – ca. 100 Ma. Again, these estimates were in agreement with Kelvin’s original age estimates for the Earth and sun. Some geologists were ready to accept an age for the Earth of ca. 100 Ma and do their best to fit all of Earth history into this “modest” time frame. However, Kelvin, Tate, King, and others kept reducing their estimates (still based on calculations of heat loss), limiting the age of the Earth and sun to only 10–40 Ma. As mentioned earlier, Kelvin’s final word on the subject in 1897 was that Clarence King’s 24 Ma age for the Earth, published in 1893, was the best available.

However, the scientific world was about to change dramatically. In the few years encompassing Perry’s 1895 critique of Kelvin’s assumptions, Goodchild’s 1897 estimate of the age of the Phanerozoic, Kelvin’s 1897 “final word,” and Joly’s 1899 age of the oceans, a spectacular scientific revolution was beginning. The discovery of x-rays by Roentgen in 1895 led directly to the discovery of radioactivity by Becquerel in 1896 which led, within a decade, to direct measurements of ages on minerals and rocks based on radioactive decay systems. Modern geochronology had been conceived.

General references: Albritton (1980), Burchfield (1990), Dalrymple (1991), Holmes (1913).

The Discovery of Radioactivity and the Birth of Geochronology

In the late 1800s there was a general impression in physics that all the great discoveries had been made. Younger physicists would have to be content with improving the accuracy and precision of already known physical constants. Then, late in 1895, only months after Perry had published his critique of Kelvin (and exposed the fatal flaw in Kelvin’s assumption about the Earth’s transfer of heat), Wilhelm Roentgen (1845–1923) discovered “X-rays,” penetrating rays emitted from a cathode ray tube. X-rays became an overnight sensation – “radiographs” showing the bones inside the hand of a live human being must have seemed absolutely magical; the general public was enthralled. The scientific community also was invigorated by this completely unexpected development. Well, most of the scientific community: “Kelvin was not moved. He had regarded the original announcement of Roentgen’s x-rays as a hoax” (Albritton 1980, p. 204). To be fair, an 1896 X-ray image of Kelvin’s own hand exists, so he soon accepted Roentgen’s discovery. One of the many scientists who did pay close attention to Roentgen’s discovery was physicist Henri Becquerel (1852–1908). To quote from a summary by Mattinson (2013a, p. 2):

Following in his father’s footsteps, Becquerel had conducted research in phosphorescence, the property of some materials, including some uranium compounds, to emit light after exposure to sunlight or ultraviolet light. However, by 1895, the 43-year-old Becquerel evidently had been inactive in research for about five years. The discovery in late 1895 by Wilhelm Roentgen of ‘X rays’ emitted from a cathode-ray apparatus spurred Becquerel back into action. Becquerel began experiments on some of his phosphorescent uranium samples to determine if they might emit not just visible light, but also invisible penetrating rays similar to Roentgen’s X-rays.

Becquerel placed photographic plates that he had wrapped in heavy black cloth on a south-facing windowsill and placed uranium samples on top of the covered photographic plates. After exposure of the uranium samples to sunlight, Becquerel developed the plates to see if any rays from the uranium had penetrated the black paper and exposed the plate. Fortune smiled on Becquerel. First, some of his previous phosphorescence work had been on uranium compounds. Of all the elements, only uranium and thorium and radioactive “daughter” elements produced by their decay generate strong penetrating radiation. If Becquerel had not had U or Th samples available, all his results would have been negative. Instead, he almost immediately obtained positive results – the plates had been exposed, producing fuzzy images the shape of the samples placed on the plates. Second,

Becquerel initially assumed that activation by exposure to sunlight was necessary for any penetrating rays to be produced, by analogy with true phosphorescence. However, for reasons that have never been clear (e.g., Badash 1996), after a period of dark, rainy weather, Becquerel developed some photographic plates, even though the uranium samples had *not* been exposed to sunlight – they had been left in a closed drawer, on top of the covered photographic plates. The photographic plates showed the same degree of exposure as before. Becquerel realized that the exposure was not related to activation by sunlight, but was an inherent property of the uranium samples. The new form of radiation, initially referred to variously as “uranium-rays” or “Becquerel-rays,” was later called “radioactivity” by Marie and Pierre Curie. That name would stick.

Initially, Becquerel’s discovery was greatly overshadowed by Roentgen’s discovery of X-rays. It was not immediately apparent that Becquerel had discovered an entirely different phenomenon, and scientists were slow to enter the new field of radioactivity. Quinn (1995, p. 143) in her excellent book on Marie Curie comments:

Becquerel himself seems to have concluded that the subject was exhausted: after his initial papers in 1896, he published only two in 1897 and none the following year. By early 1898, as science historian Lawrence Badash has noted, the subject was ‘something of a dead horse.’ Other than Becquerel’s papers, only four were devoted to the uranium rays at the Academy in the year of their discovery. In contrast, Gustave LeBon’s false claims for ‘black light’ were the subject of fourteen papers. And Roentgen’s X rays got the most attention of all. Nearly one hundred papers were delivered at the Academy in 1896 concerning X rays.

In this respect it seems particularly ironic that one of the very few scientists who took any interest in confirming some of Becquerel’s work was William Thomson (Lord Kelvin), then 73 years old. The general lack of interest in Becquerel’s discovery (certainly) and the fact that Kelvin, who did show interest, had, for the previous few years been somewhat of a mentor to Pierre Curie (likely) were responsible for Marie Curie choosing to study radioactivity for her Ph.D. project, starting in 1898. Marie soon found that the mineral pitchblende (uranium oxide) was several times more radioactive than pure uranium metal. This led her to discover two new radioactive elements, radium (Ra) and polonium (Po), both decay products of uranium. She then concentrated Ra for chemical characterization and further study. Marie’s meticulous work and exciting discoveries inspired others to enter the field:

In a series of brilliant papers in 1902, Ernest Rutherford and Frederick Soddy established that radioactivity resulted from the transformation of unstable elements into new forms. A competing theory, that radioactive elements were somehow absorbing then releasing energy from outside sources, soon died out. Rutherford and Soddy derived the mathematical principles of radioactive decay and suggested that helium (He) was a stable daughter product of U decay. Rutherford realized that the ratio He/U could be used to measure the ages of geological materials and presented the first dates based on radioactive decay in a 1904 lecture. (Mattinson 2013b, p. 53)

Modern geochronology was born.

Meanwhile, in 1903, Pierre Curie and Albert Laborde discovered that the radioactive decay of Ra produced enormous amounts of heat, invalidating Kelvin’s assumption of a simple cooling Earth with no internal heat source (more on this later). The discovery inspired a flurry of letters to *Nature* in 1903. W. E. Wilson, an independent “gentleman-astronomer” (Letter to the Editor, July 9, 1903) enthusiastically suggested that if the sun contained 3.6 g of radium per cubic meter, its entire energy output could be provided by the radioactive decay of radium (later, Joly and Rutherford would point out that to support this concentration of radium, the sun would have to be made up almost entirely of uranium!). George Darwin was more nuanced in a September 16, 1903, letter: “Knowing as we now do, that an atom of matter is capable of containing an enormous store of energy in itself, I think we have no right to assume that the sun is incapable of liberating

atomic energy to a degree at least comparable with that which it would do if made of radium.” John Joly also weighed in, commenting on the effects of heat from radioactive decay in the sun and the Earth in an October 1, 1903, letter: “. . . it would appear that the estimates derived from physical speculations are now subject to modification in just the direction which geological data required. The 100 million years which the doctrine of uniformity requires may, in fact, yet be gladly accepted by the physicist.” Note: Joly’s enthusiasm for methods based on radioactive decay dimmed when the first He/U and Pb/U dates indicated that Joly’s own method greatly underestimated the age of the Earth.

The year 1903 was also the year that the Nobel Prize in physics was awarded jointly to Henri Becquerel, Pierre Curie, and Marie Curie for their work on radioactivity. Radium, radiation, and the Curies quickly acquired superstar status. In the geological community, the enthusiasm for radium, along the lines of the *Nature* letters quoted above, promoted a myopic focus on radiogenic heat production as dealing the fatal blow to Kelvin’s four-decade dominance of the age of the Earth debate. This view is still promoted in many elementary texts, e.g., “Perhaps the most durable myth in elementary Earth science texts is the view that the discovery of radioactivity . . . and radioactive heat generation . . . forever ended the late nineteenth century controversy involving Lord Kelvin and the age of the Earth” (Harrison 1987). A most unfortunate side effect was that John Perry’s devastating (and much more correct) 1895 critique of Kelvin’s model sank into obscurity and remained there until relatively recently. A modern analysis of Kelvin’s approach to the age of the Earth demonstrates that Perry had it right:

. . . even if Kelvin had included a reasonable radiogenic heat production in his thermal evolution models, he would still have found grounds for arguing that the age of the Earth was on the order of 10^8 years. The essential missing process *is not really radiogenic heating at all but thermal convection*, which allows the surface flux to exploit the entire heat of the Earth as opposed to simply that of a shallow conductive boundary layer. (Richter 1986, p. 397, emphasis added)

But Richter inexplicably makes no reference to Perry, even though Perry’s contributions are thoroughly covered in the 1975 first edition of Burchfield’s book, which Richter cites as a general reference for the age of the Earth controversy. This oversight was pointed out by Harrison (1987) and corrected in later papers by Richter and his colleagues. “If the scientific community of the day had absorbed Perry’s message. . . The realization that convection takes place within the Earth’s apparently solid interior would have made it hard to sustain the “fixist” view of the Earth—which held that it was physically impossible for continents to move horizontally. That perception of fixity exerted a powerful brake on geological progress in the first half of the 20th century. . .” (England et al. 2007, p. 349).

Within a few years of the paper on radium heat production by Curie and Laborde and the Nobel Prize for Becquerel and the Curies, the first dates of geologic materials based the decay of uranium to helium were formally published by Rutherford in 1906 and those based on the decay of uranium to lead (the ultimate stable end-product of the uranium “decay series”) were published by Bertrand Boltwood in 1907, demonstrating that Paleozoic and Precambrian rocks ranged from hundreds of millions to billions of years old. Lord Kelvin died in 1907, but not before reasserting his belief that gravity was the only possible source of the heat of the Earth and sun, and suggesting “. . . that somehow ethereal waves may supply the energy to the radium as it is giving out heat to the ponderable matter around it” (Burchfield 1990, p. 165). This was a version of an idea held for a time by Becquerel and the Curies, the phosphorescence model, that the energy released by radioactive decay had somehow been absorbed from outside forces. With Kelvin’s death, one might have imagined that the geological community would have embraced the new field of geochronology with great enthusiasm. This would be a mistake. First, radioactivity had been discovered and

studied by physicists and chemists, who also presented the first dates based on radioactive decay. Having been burned once by the physicists (Kelvin et al.), geologists were wary:

Radioactive dating clearly had not taken geology by storm. As Joseph Barrell succinctly summarized the situation in 1917: ‘After one experience with the fallibility of physical argument notwithstanding its mathematical character, it would certainly be unwise for geologists to accept unreservedly the new and larger measurements of time given by radioactivity. There may be here, also, factors undetected and unsuspected which vitiate the results’. (Burchfield 1990, p. 190)

Second, some geologists had a considerable intellectual investment in their own earlier estimates of the age of the Earth. For example, Joly’s 100 Ma age based on the salinity of the oceans had gained him considerable attention and prestige, especially after heat from radioactive decay seemed to invalidate Kelvin’s most recent younger estimates of the age of the Earth. Only a couple of years later, ages based on radioactive decay published by Rutherford and Boltwood appeared to demolish Joly’s 100 Ma figure. Joly denied the validity of radiometric ages for more than two decades. “It was not until 1930 that he showed any sign of actually yielding to the accumulated mass of radiological evidence, and like Kelvin he died without publicly relinquishing his convictions” (Burchfield 1990, p. 189). By then, Rutherford and Boltwood had long since left the field of geochronology, having returned to their main interests in the physics of matter and radioactive decay, and the chemistry of the U and Th decay series, and new giant in the field of geochronology had emerged – Arthur Holmes.

General references: Albritton (1980), Badash (1996), Burchfield (1990), Dalrymple (1991), Holmes (1913), Quinn (1995), Rhodes (1986).

Arthur Holmes and the Growth of Geochronology

Arthur Holmes (1890–1965) was a small boy when radioactivity was discovered, and a teenager when the first He/U and Pb/U dates were published. He grew up with the excitement of the dawning of a new scientific era. Holmes attended a “higher grade school” with a strong science orientation, and an exceptional physics teacher who used geological examples in many of his lectures. In 1906 Holmes was mesmerized by an exchange of letters in *The Times of London*. Kelvin initiated the exchange after he read a report in *The Times* about new experiments on radioactivity by Soddy and William Ramsay:

Kelvin wrote an angry letter to *The Times* criticizing their work. . . .he also considered it added nothing new to the theory of atoms that had been proposed by Democritus two and a half thousand years ago! The irritation felt by the younger generation by Kelvin’s obstinate refusal to accept the new evidence was thinly veiled: ‘Lord Kelvin’s letter will of course receive respectful attention. . .but it is also known that his brilliant original mind has not submitted patiently to the task of assimilating the work of others by the process of reading’. (Quinn 1995, pp. 11–12)

The bare-knuckles match went on for over a month, with Kelvin on one side, and the young lions of radioactivity on the other: Ramsay, Rutherford, Soddy, and Robert Strutt (the latter having narrowly missed becoming the first to publish an age based on the accumulation of helium from U decay). Holmes was hooked!

In 1907 Holmes started to study physics at the Royal College of Science, London. In his second year, Holmes renewed his interest in geology thanks to a brilliant and dynamic young geology professor, William Watts. After Holmes’ second year, he switched his emphasis to geology. Another young professor at the Royal College of Science was none other than Robert Strutt. Holmes recognized a splendid opportunity to combine his interests in geology and radioactivity

and began a research project developing improved Pb/U dating techniques under the direction of Strutt. The timing was particularly fortuitous, as Boltwood had returned to his primary research interest on the chemistry of the uranium and thorium decay series, leaving the newly born field of Pb/U geochronology wide open. Almost immediately, Holmes made a series of important contributions. He developed more sensitive chemical and radiochemical techniques for the measurement of U and Pb than those used by Boltwood. Whereas Boltwood had been limited to U-rich ore minerals, Holmes could analyze minerals much lower in U and Pb such as zircon and even feldspar. Using an updated decay constant for U, Holmes published a series of new Pb/U analyses and dates and also recalculated Boltwood's earlier Pb/U dates. Arthur Holmes, the physicist, might have stopped there, but Arthur Holmes, the geologist, investigated the geological settings of all the samples dated and produced the beginnings of a geologic time scale in 1911. Holmes' results are remarkable in that they are all in general agreement with modern results: Carboniferous ca. 340 Ma, Devonian ca. 370 Ma, "pre-Carboniferous" ca. 410 Ma, "Silurian or Ordovician" ca. 430 Ma, and Precambrian ca. 1,025–1,640 Ma. Holmes published a 196 p. monograph in 1913 boldly titled "The Age of the Earth." The book provides a summary of early efforts to determine the age of the Earth and gives a flavor of the commonly bitter controversies that surrounded these efforts. As discussed above, some of the same geologists who considered Lord Kelvin's estimates of the age of the Earth to be much too young now objected to minimum ages for the Earth based on radioactive decay systems as being much too old. Holmes hoped to use his book to convince the geological community of the fundamental accuracy of geochronology based on radioactive decay. Summarizing all the available He/U and Pb/U dates, Holmes presented an expanded version of his geologic time scale, from Pleistocene to Precambrian. For Holmes, this was only the beginning of a long and remarkable career devoted to expanding and improving the dating of the geologic time scale and determining the age of the Earth itself.

General references: Holmes (1913), Lewis (2000), significant parts of this section are adapted with slight modification from Mattinson (2013a, 2013b).

The Discovery of Isotopes and Early Isotopic Research

As might be expected, the discoveries of x-rays, radioactivity, and the radioactive transmutation of atoms into different forms had far-reaching effects, inspiring a great outburst of research on the nature of matter itself. In 1911 Rutherford discovered the atomic nucleus by bombarding thin metal foils with collimated beams of alpha particles. Highly accurate measurements revealed that the atomic weights of many elements were not whole numbers. In particular, in 1913, T. W. Richards measured the atomic weight of Pb produced by the decay of U and found that it was significantly lower than the atomic weight of "ordinary" Pb. Innovative instrumentation played an increasingly vital role. J. J. Thomson (Rutherford's professor) built a "positive ray" apparatus, a simple antecedent to today's mass spectrometers. Thomson discovered that neon had two different forms – one with a mass of about 20 and another with a mass of about 22. Soddy coined the term "isotopes" for these atoms of the same element but with different atomic masses. The neutron was suggested by Rutherford in 1920 (later confirmed experimentally by Chadwick in 1932), fleshing out the basic picture of the atomic nucleus. In 1920, F. W. Aston built an advanced version of Thomson's "positive ray" instrument. Aston's "mass spectrograph" used photographic plates to record the mass spectra of elements and allowed semiquantitative measurements of isotopic ratios. After confirming Thomson's work on neon, Aston went on to investigate the isotopic composition of many elements over his career, including "ordinary" Pb from Pb ore samples in 1927 and

“radiogenic” Pb from a U ore sample in 1929. Pb from the U ore unexpectedly contained ^{207}Pb . This discovery led to the inference that U contained not just ^{238}U , but also a minor, previously unknown isotope that was the parent of ^{207}Pb , i.e., ^{235}U . J. L. Rose and R. K. Stranathan in 1936 realized that the different decay rates for ^{238}U and ^{235}U required that the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of Pb produced by uranium decay increase with increasing age – an age could be determined for a uranium-bearing mineral simply from the lead isotopic composition alone. Thus the foundation for modern isotope geology and geochronology was laid.

General references: Harper (1973), significant parts of this section are adapted with slight modification from Mattinson (2013a, 2013b).

Alfred Nier, Isotopes, and Mass Spectrometry

Over the next several years, improvements in instrument design resulted in the “mass spectrometer” in which photographic plates were replaced by collection and electronic amplification of the small electrical currents produced by the beams of positively charged ions of each isotope. The technological advance allowed much more precise and accurate isotopic measurements. Alfred Nier not only made major contributions to mass spectrometer design but also made several discoveries that were critical to advances in geochronology. Nier in 1938 found that “common lead,” e.g., lead from lead ores, had significant variations in isotopic compositions. Earlier measurements of the mean atomic mass of lead from a variety of ore samples gave essentially identical results, leading to the assumption that all common leads must have ca. identical isotopic compositions. Nier demonstrated that relative to the non-radiogenic isotope, ^{204}Pb , ^{206}Pb , and ^{208}Pb tended to vary in a highly correlated way that fortuitously resulted in little or no variation in mean atomic mass. Nier further suggested that common lead must consist of a mixture of primeval lead of fixed isotopic composition dating to the time of the Earth’s formation, plus radiogenic lead generated by the decay of uranium and thorium after the Earth’s formation. This was a conceptual leap crucial to all subsequent estimations of the age of the Earth. In 1939 Nier turned his attention to uranium and lead in uranium ores, making a remarkably accurate measurement of the $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios of uranium. Nier then combined the uranium isotope data with the lead isotope data from the same samples to calculate a remarkably accurate decay constant for ^{235}U . In 1941, Nier and his collaborators reported a $^{207}\text{Pb}/^{206}\text{Pb}$ age of ca. 2.6 Ga for a monazite from Manitoba, Canada. This was the first *isotopic* age determination for the antiquity of the Precambrian, and a rigorous minimum age for the Earth. Nier and his colleagues also reported lead isotope measurements for a wide array of lead ores. These data attracted the attention of E. K. Gerling, Arthur Holmes, and F. G. Houtermans all of whom realized that Nier’s isotopic data for lead ores could be used to estimate the age of the Earth. Gerling, Holmes, and Houtermans calculated ages for the Earth ranging from ca. 3.0 to 3.9 Ga on the (incorrect) assumption that the ore with the lowest $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios approximated the isotopic composition of primeval lead. At this stage in the evolution of geochronology, isotope ratios were being measured by more or less modern techniques, but the amounts of uranium and lead were still measured by classical chemical methods. This was about to change dramatically.

General references: Harper (1973), significant parts of this section are adapted with slight modification from Mattinson (2013a, 2013b).

The Discovery of Nuclear Fission and the Separation of Isotopes

Meanwhile, other momentous discoveries in nuclear physics were underway which would have profound implications for geochronology, both directly and indirectly. In 1933, only months before Marie Curie's death, her daughter and son-in-law, Irene and Frederic Joliot-Curie, bombarded aluminum with alpha rays. The aluminum captured alpha particles and emitted neutrons, producing a radioactive isotope of phosphorous. The phosphorous in turn decayed with a short half-life to a stable isotope of silicon. The Joliot-Curies had artificially transformed a stable element into a different, radioactive element. Many labs began bombarding a wide range of elements with various particles, including neutrons. Irene Joliot-Curie and Pavel Savitch, a visitor to her lab, bombarded uranium with neutrons and produced a radioactive product that appeared to have the properties of lanthanum. Conventional wisdom at the time dictated that products of irradiation should be within a few atomic mass units (amu) of the target element. Since lanthanum is ca. 100 amu lighter than uranium, the Joliot-Curie-Savitch result seemed highly unlikely, in fact impossible, even to Joliot-Curie and Savitch themselves. Had they been bolder, they might have realized that they had induced nuclear fission. The Germans Otto Hahn and Fritz Strassmann, who also doubted the original result, duplicated the experiments. They eventually positively identified barium (also about 100 amu lighter than uranium), plus several other elements, as products of the neutron irradiation – clear evidence that the atom had been split. The discovery of fission triggered another period of intense research, and with the onset of World War II, the “Manhattan Project,” and the development of nuclear weapons. An essential part of the Manhattan Project was development of isotope separation techniques to concentrate ^{235}U , the isotope of uranium susceptible to “induced fission” by neutron irradiation. The ability to separate isotopes would open the door to a major breakthrough in geochronology, the “isotope dilution method” for precise and accurate measurements of very small amounts of a wide range of elements.

General references: Harper (1973), Quinn (1995), Rhodes (1986), significant parts of this section are adapted with slight modification from Mattinson (2013a, 2013b).

The Isotope Dilution Method and the Development of Geochronology

After World War II many scientists recognized that the discoveries of military research could be applied to a wide range of research problems in physics, chemistry, and geology. One such scientist was Harrison Brown, who headed a group at the University of Chicago studying trace elements in meteorites. In addition to his interests in meteorite chemistry in general, Brown was familiar with the recent work on the age of the Earth using Pb isotopes. He thought that iron meteorites might contain Pb but not U, thus providing a true primordial isotopic composition of Pb from the early solar system. Key members of the group included Mark Ingram, a physicist and mass spectrometer expert, and graduate students Clair “Pat” Patterson and George Tilton. The group developed new, much more sensitive mass spectrometric techniques for measuring the isotopic compositions of small amounts of lead in meteorites and minerals from terrestrial samples (e.g., the mass spectrometry methods they developed reduced the amount of Pb needed for analysis by a factor of ca. 1,000 compared with Nier's earlier work). Brown's group also perfected the isotope dilution (ID) technique for accurately measuring low concentrations of Pb, Th, and U. In the ID technique, a known amount of a highly purified isotope of the element of interest is added to a sample, prior to any chemical separations. For example, a known amount of highly pure ^{235}U is added to a sample containing natural U, which is over 99 % ^{238}U . After separating U from all of the other elements in

the sample, the ratio of $^{235}\text{U}/^{238}\text{U}$ is measured by mass spectrometry, and the amount of ^{238}U in the sample can be calculated with high accuracy. The same approach is used for Pb, using a “tracer” or “spike” of a highly purified isotope of lead. The work led by Tilton on minerals such as zircon, sphene (titanite), apatite, and several other minerals from terrestrial granite was an immediate success, and fully published after some delay owing to “top secret” classification of the very existence of purified ^{235}U (Tilton et al. 1955). The Pb isotopic work on meteorites went more slowly owing to low Pb levels in most meteorite samples and high levels of Pb contamination in the environment. Patterson continued with the meteorite work, overcame the challenges of Pb contamination, and determined a ca. 4.55 Ga age for meteorites and the Earth (Patterson et al. 1955; Patterson 1956), quite compatible with modern measurements. The long quest to determine the age of the Earth had finally succeeded.

General references: Harper (1973), Lewis (2000), significant parts of this section are adapted with slight modification from Mattinson (2013a, 2013b).

50 Years of Refinement, Expansion, and Growth of Geochronology

At about the same time that Brown’s group developed the next generation of U–Th–Pb geochronology, similar techniques using advanced chemical separation, mass spectrometry, and isotope dilution were applied to the Rb–Sr and K–Ar parent-daughter systems. Rb and K were discovered to be “weakly radioactive” by 1906 but could only be exploited for geochronology by about the 1950s when instrumentation and methods had sufficiently improved. Also developed in the early 1950s was the carbon-14 dating method. By the mid-1960s these techniques were all well established.

The fifty years between 1963 and the present have seen, quite literally, an explosion in the amount of geochronological research, the diversity of methods, the quality of the analyses, and the sophistication of data interpretation. Major driving forces have included development of new instrumentation, analytical techniques, data analysis techniques, and, especially in the last decade, laboratory collaboration at national and international levels. ... depending on how one counts, close to 40 different dating methods are now available, spanning age ranges from months to billions of years. (Mattinson 2013a, pp. 5, 10)

Any detailed discussion of all these methods is far beyond the scope of this historical review. Interested readers can find more breadth and detail in the following sources: (1) general information, Allègre (2008), Dickin (2005), Faure and Mensing (2005); (2) recent publications, mostly on state-of-the-art techniques plus some history, Amelin and Ireland (2013), Condon and Schmitz (2013), Corfu (2013), Mattinson (2013a, 2013b), Nemchin et al. (2013), Schmitz and Kuiper (2013), and Schoene et al. (2013); and cross-references.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Fission Track Dating](#)
- ▶ [Geochronology](#)
- ▶ [Geological Time Scale](#)
- ▶ [Lu-Hf Dating](#)
- ▶ [Re-Os Dating](#)

- [Rb-Sr Dating](#)
- [U Series Dating](#)
- [Uranium-Lead Dating](#)
- [U-Th:He Dating](#)
- [Zircon](#)

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Zircon

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Synonyms

[Cyrtolite](#); [Zirconium silicate](#)

Zircon (ZrSiO_4) is a common accessory mineral found throughout a wide range of igneous, metamorphic, and sedimentary rock types and unconsolidated sediments (e.g., beach or river sands). Zircon crystallizes in the tetragonal crystal system and contains the SiO_4 tetrahedra as the framework of its crystal structure. As such it is classified as an orthosilicate (or nesosilicate) mineral (Finch and Hanchar 2003) (Fig. 1).

A highly refractory mineral, zircon is resistant to chemical and physical weathering and chemical alteration over a wide range of pressures and temperatures in different geological environments. It often preserves geochemical information from multiple geologic events (e.g., internal structures and zoning) revealed using cathodoluminescence (CL) and back-scattered electron (BSE) imaging (Corfu et al. 2003) (Fig. 2).

Zircon often incorporates trace to minor element levels of non-formula elements, such as Hf, the rare-earth elements (REE) including Y, P, U, and Th in its crystal structure (Speer 1982; Hoskin and Schaltegger 2003). The Th/U ratio, for example, has been used to classify zircon as being igneous ($\text{Th/U} > 0.2$) or metamorphic ($\text{Th/U} < 0.1$) (Hartmann and Santos 2000); however, there are many exceptions to this rule. In particular, if other Th-rich minerals, such as monazite or allanite, crystallized prior to or at the same time as the zircon, those phases would preferentially incorporate Th over U and thereby change the amount of Th available for the zircon. This in turn would result in a lower Th/U ratio than would be expected.

Due to its sluggish diffusivity for virtually all impurity trace elements (Cherniak 2010), zircon retains a remarkable amount of geochemical information about the source region in which it crystallized (e.g., Speer 1982; Hoskin and Ireland 2000; Hanchar and van Westrenen 2007). The REE composition, for example, has been used to constrain the petrogenesis of zircon. In particular, using differences in the slope of the REE pattern for the heavy REE (HREE) on lognormal chondrite-normalized plots, it has been shown that zircon that crystallized in igneous environments has a steeper slope for the HREE than zircon that crystallized in high-grade metamorphic environments (Rubatto 2002; Rubatto and Hermann 2003; Whitehouse and Platt 2003).

Zircon is the premier mineral of choice for U-Th-Pb geochronology because common lead (i.e., ^{204}Pb) is excluded from its crystal structure during crystallization, whereas radiogenic Pb produced from the radioactive decay of U and Th is retained (Davis et al. 2003). This is due to the extremely sluggish diffusivity of Pb in crystalline zircon. Once zircon becomes metamict, however, the diffusivity increases which in turn allows the Pb ions to more readily diffuse out of the zircon

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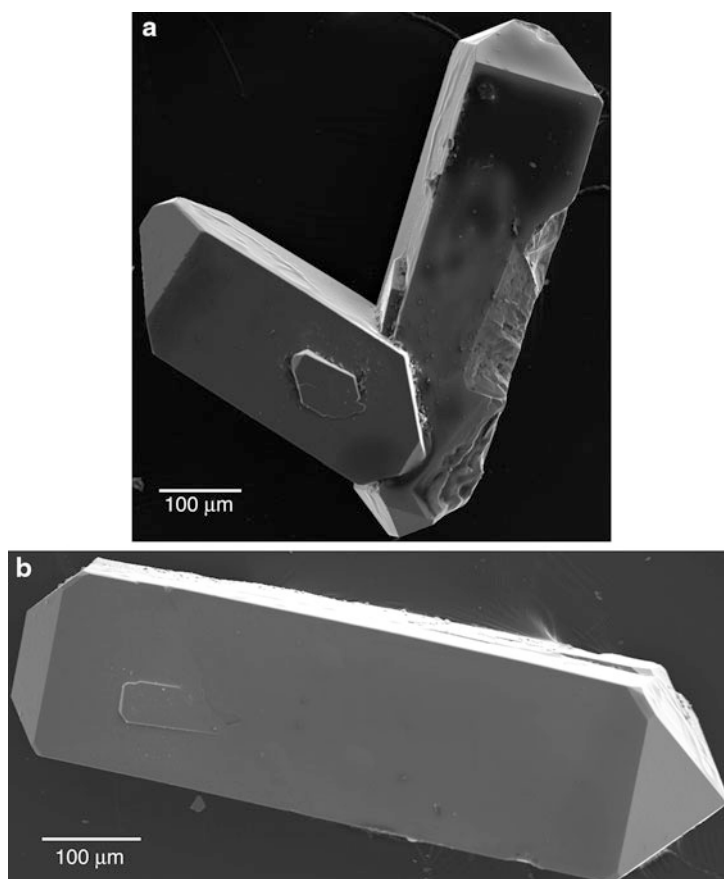


Fig. 1 Secondary electron images of synthetic rare-earth element (Er) and P-doped zircon crystals. (a) Twinned crystals. (b) Single crystal

structure (Cherniak 2010). The effects of this damage can be quantified using Raman spectroscopy (Nasdala et al. 2006).

The physical and chemical durability of zircon is a major factor in it being the mineral by which many of Earth's oldest known rocks have been dated (e.g., Froude et al. 1983; Bowring et al. 1989; Wilde et al. 2001) and is also an important factor in zircon having been previously considered as a candidate ceramic waste form for the geologic disposal of excess plutonium from dismantled nuclear weapons (Ewing et al. 2003).

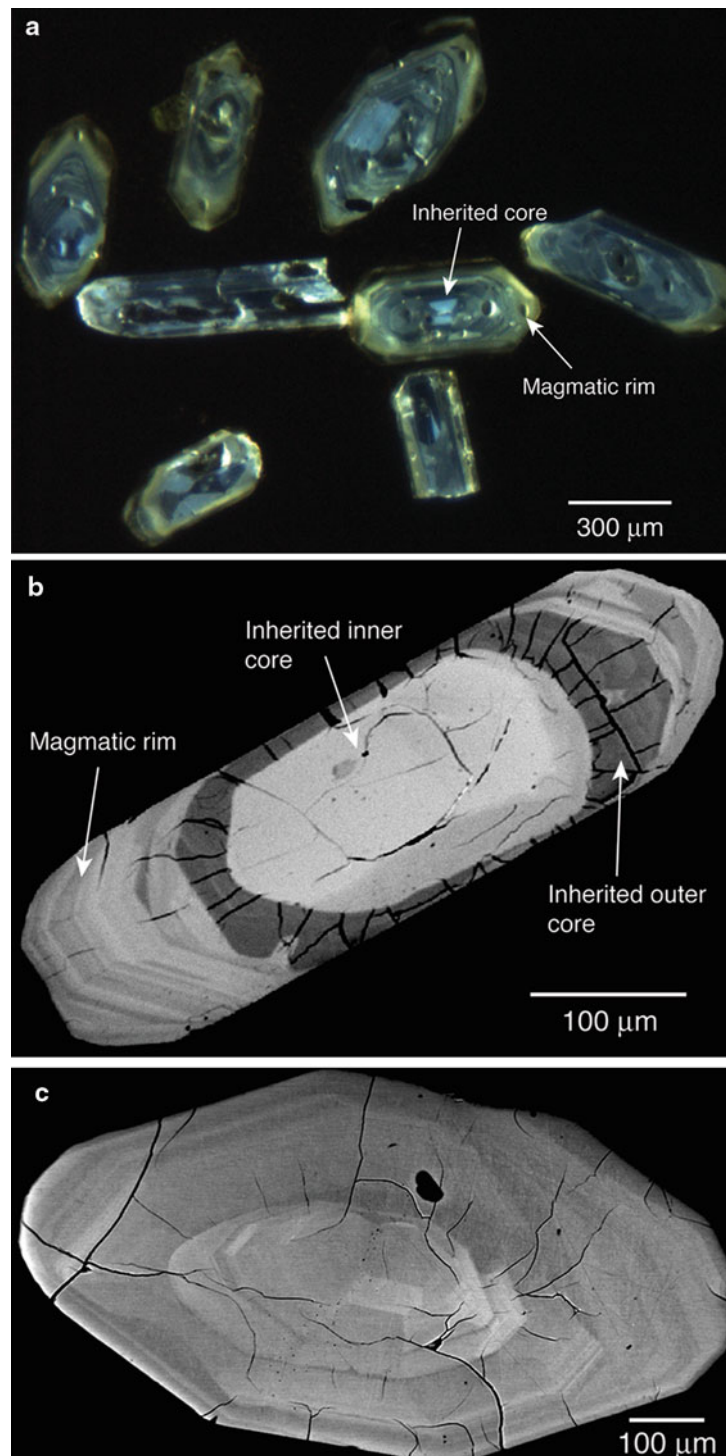


Fig. 2 Cathodoluminescence (CL) and back-scattered electron (BSE) images of natural zircon crystals mounted in epoxy and polished to reveal the crystal interiors. **(a)** CL image of zircon crystals from a tonalite from Adamello, Italy, with magmatic rims and inherited cores. **(b)** BSE image of zircon with inherited inner and outer cores and younger magmatic overgrowth from the Adirondack Mountains, New York State. **(c)** BSE image of a detrital zircon from a placer heavy-mineral sand deposit in North Carolina with possible inherited core (but this grain has not been dated so it is not possible to say for sure)

Cross-References

- ▶ [Acasta Gneiss](#)
- ▶ [Earth Formation](#)
- ▶ [Earth's Oldest Rocks](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)
- ▶ [Historical Development \(of Dating Methods\)](#)
- ▶ [Jack Hills Zircon](#)
- ▶ [Crustal Evolution](#)

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Amino Acid Racemization, Coastal Sediments

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Introduction

Amino acid racemization (AAR) dating has been applied to a large variety of coastal sediments representing a range of geological ages and depositional environments (Fig. 1). In most cases, samples analyzed for the extent of racemization are of biogenic origin (mollusks, foraminifera, mixed carbonate sediments, or corals). AAR has been applied to coastal sediments as young as a few hundred years and as old as several million years. The goals of these studies include as follows: (1) correlation and relative age assignments for Pleistocene coastal or shallow marine units, (2) assessing Quaternary tectonic deformation rates and/or relative sea-level histories, (3) deciphering the chronology of Pleistocene glacial advances in coastal regions, and (4) understanding Holocene sedimentary processes including age mixing. In most cases, multiple samples of different genera have been analyzed from each collection site, and relative ages are inferred from apparent clusters of D/L values (aminozones).

Topics reviewed here include the following categories, with representative references: (1) emergent deposits, active continental margins, such as the Mediterranean (Hearty et al. 1986, 2007) and the Pacific coasts of South America (Hsu et al. 1989) and North America (Wehmiller 2013); (2) emergent deposits and passive continental margins, such as Australia (Murray-Wallace 1995, 2000) and the Atlantic coasts of South America (Aguirre et al. 1995) and North America (Wehmiller 2013); (3) offshore deposits and passive margins (Murray-Wallace et al. 2005; Meijer and Cleveringa 2009; Wehmiller et al. 2010); (4) tropical islands and carbonate reefs (Hearty et al. 2007); (5) coastal regions affected by glaciations (Miller and Mangerud 1985; Kaufman and Brigham-Grette 1993; Refsnider et al. 2013); and (6) age-mixing studies in coastal regions (Wehmiller et al. 1995; Kosnik et al. 2009). The latter three topics are discussed in more detail in other entries (see ► [Eolianites](#), [Arctic](#), [Biostratigraphy](#)). AAR results are used to determine relative ages within a study region, but if associated with independent age calibrations (derived from U–Th, ^{14}C , or other numerical dating method), then AAR can be used to provide semiquantitative ages using appropriate model(s) for the overall kinetics of racemization.

AAR Studies of Active Continental Margins

Along the Pacific coast of North America, south of Cape Mendocino, strike-slip relative motion is related to the northwest motion of the Pacific Plate. Coastal units and marine terraces in this region usually record relatively low uplift rates (approx. <0.2 m/ka years) with a few notable exceptions in localized areas. North of Cape Mendocino, where plate convergence related to spreading from the Juan de Fuca Ridge dominates the region, ages for uplifted marine terraces suggest more

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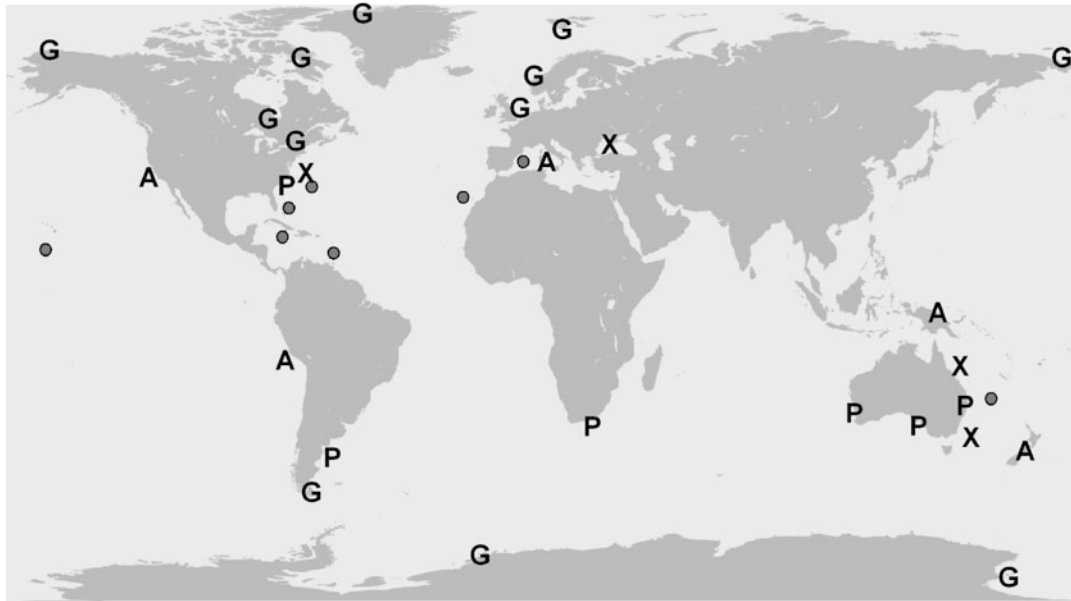


Fig. 1 World map showing coastal regions where AAR studies have been conducted. Letters on map denote the following: A, active margins; P, passive margins; G, coastal areas influenced by glaciations; X, offshore studies. Solid circles on map identify tropical islands for which AAR data exist

variable uplift rates, occasionally as high as 1 m/ka years (Kennedy et al. 1982; Dupré et al. 1991; Muhs et al. 1992a, 2004).

Uranium-thorium dating of solitary corals has been applied to numerous marine terrace sites along the North American Pacific coast (Muhs et al. 2004). These U–Th results provide rigorous calibration for the regional aminostratigraphy, allowing age estimates for AAR results from other sites with no independent age control. Two fundamental principles regarding racemization were tested and evaluated using samples from Pacific coast terraces (Wehmiller et al. 1977; Kennedy et al. 1982): (1) D/L values in multiple taxa increase with increasing terrace elevation for vertical sequences of terraces, and (2) D/L values increase with decreasing latitude (increasing temperature) in samples of known equal age. Molluscan faunal assemblages indicative of local water temperatures at the time of formation of late Pleistocene terrace deposits also are age indicative because of their association with the marine climate record and associated calibrated AAR results (Kennedy et al. 1982). The original aminostratigraphic framework (Kennedy et al. 1982) was extended with results from uplifted terraces on the Baja California Peninsula (Keenan et al. 1987) and the Gulf of California (Ortlieb 1991). Regionally specific studies of AAR in uplifted terraces in Southern California include Santa Barbara County (Rockwell et al. 1992), the Palos Verdes Hills (Muhs et al. 1992b), and San Diego County (Kern and Rockwell 1992). Localized zones of unusually rapid uplift rates (up to ~5 m/ka) are inferred from the ages (AAR, C14, and U–Th) of terraces found along the northern margin of the Santa Barbara Channel (Wehmiller 1992, 2013).

The marine terraces along the South American Pacific coast between ~15° and ~30° S are influenced by the subduction of the Nazca Plate beneath the South American Plate. In the northern area (Peru) six distinct aminozones, estimated to represent ages up to ~900 ka, are recognized, with independent calibration using electron spin resonance (ESR) dating (Hsu et al. 1989). In the more southern region (northern and central Chile), five aminozones were recognized, the oldest estimated to represent an age of ~700 ka (Hsu et al. 1989). In several cases, multiple aminozones were identified within a single localized terrace sequence. The highest uplift rates in Peru (~0.5 m/ka) are

found where the Nazca Ridge is being subducted under that South American Plate (Hsu et al. 1989; Hsu 1992; Goy et al. 1992; Saillard et al. 2011). Uplifted terraces are highest above the southern flank of the Nazca Ridge, being lower both to the north and south of the local region of ridge subduction. To the south, terrace uplift rates are generally less than 0.2 m/ka (Hsu 1992; Ortlieb et al. 1996). In some cases these low uplift rates have resulted in terrace reoccupation, with deposits of at least two interglacial ages being found within what appears to be a single mapped morphologic unit (Leonard and Wehmiller 1992).

A broad regional study of AAR data in mollusks (*Glycimeris* and *Arca*) from uplifted marine deposits in the western and central Mediterranean spans a latitude range of $\sim 10^\circ$ and a longitude range of $\sim 25^\circ$ (Hearty et al. 1986). The AAR data cluster into five distinct aminozones, the second youngest being associated with four U–Th coral ages that cluster around 126 ± 7 ka, equivalent to marine isotope substage 5e (Hearty et al. 1986). More detailed studies of selected sites in the western Mediterranean (Torres et al. 2000, 2013) using modern analytical methods (see ► [Chromatography](#)), while consistent with the fivefold aminostratigraphy, indicate that variability in D/L values within an aminozone can occur because of age mixing and/or shell alteration.

Coastal Quaternary units are preserved intermittently around the North and South Islands of New Zealand, where active subduction and strike-slip faulting occur associated with the convergence of the Australian and Pacific Plates. AAR data from these sites were occasionally obtained on wood (Pillans 1990) but more often using marine mollusks (Ota et al. 1996; Bowen et al. 1998). Along the south shore of the North Island of New Zealand, up to four kilometers of Plio-Pleistocene sediments are exposed in the Wanganui Basin with at least five aminozones representing deposition over the past one million years (Bowen et al. 1998). Supporting chronologic data include magnetostratigraphy and fission-track dating of interbedded volcanic ashes. At least seven nearby uplifted marine terraces can be correlated with portions of the Wanganui section using associated AAR data (Bowen et al. 1998), and similar correlation can be made with aminozones on the South Island of New Zealand (Ota et al. 1996).

AAR Studies of Passive Continental Margins

The Atlantic margin of the United States ($\sim 45^\circ$ N to $\sim 24^\circ$ N) includes sites of some of the earliest AAR studies of Quaternary marine mollusks (Mitterer 1974; Muhs et al. 2004; Wehmiller 2013). Exposed Quaternary coastal units in this region occur within ~ 10 m of sea level, reflecting minimal tectonic deformation. Nevertheless, there are underlying structures that influence the pattern of Quaternary sedimentation, the Albemarle Embayment (eastern North Carolina) being one major example. The Quaternary section in the Albemarle Embayment is up to 100 m thick, thinning to no more than ~ 10 m to the north and south, over the Norfolk and Cape Fear arches, respectively. Combined U–Th, AAR, and Sr dating indicates that at least eight separate phases (aminozones) of sedimentation between ~ 2 Ma and ~ 100 ka are preserved in the Albemarle section (Wehmiller et al. 2010, 2012). To the south of the Albemarle, multiple coast parallel paleoshorelines are recognized, but fewer AAR aminozones (~ 3 – 5) are recognized, most likely because the record is thin and less complete. To the north of the Albemarle, a record of paleoshorelines and fluvial incision during multiple glacial-interglacial cycles within the Chesapeake Bay drainage system is preserved (Groot et al. 1990; Genau et al. 1994; Mirecki et al. 1995; Wehmiller 2013). Units dated by AAR in this region are found within approx. ± 5 m of present sea level. AAR data from the Delmarva Peninsula, combined with stratigraphic and geomorphic analysis, indicate that the Peninsula evolved in a southerly direction during the Pleistocene, responding to multiple cycles of fluvial incision and

valley filling during glacial-interglacial sea-level cycles. AAR data for beach shells in the US mid-Atlantic region demonstrate age-mixing processes associated with coastal dynamics and subsurface stratigraphy (Wehmiller et al. 1995).

AAR and associated radiocarbon, U–Th, or luminescence data exist for Quaternary coastal units on the western, southern, and eastern coasts of Australia, including some offshore marine cores (Murray-Wallace 1995, 2000; Murray-Wallace et al. 2001, 2005; Hearty and O’Leary 2008). AAR data for the southern coast can be grouped into at least four aminozones representing deposition during most of the Pleistocene. Whole-rock (eolianite) AAR age estimates combined with luminescence dating from the Coorong Coastal Plain and the mouth of the River Murray, South Australia, show that a series of coastal barriers have developed in this region over the past 500 ka in response to glacial-interglacial sea-level cycles (Murray-Wallace et al. 2001, 2010).

Extensive AAR data exist for coastal units on the western coast of Australia, primarily based on the analysis of eolianites, samples composed of nearly 100 % carbonate fragments (Hearty 2003; Hearty and O’Leary 2008; O’Leary et al. 2008). Six aminozones are recognized, spanning an interval from the Holocene (<10 ka) to over 500 ka. A global synthesis and discussion of the geochronology of the last interglacial (MIS 5e) shoreline (Hearty et al. 2007) include AAR data from multiple Australian sites and also sites from the central Pacific, western Atlantic, and the Mediterranean.

Hearty and Aharon (1988) and Kosnik et al. (2007, 2009, 2013) reported AAR data for samples from the Great Barrier Reef, offshore eastern Australia. These studies have focused on Holocene specimens, often using age-calibrated samples to establish the kinetics of racemization in different sample types. Kosnik’s studies also emphasize the use of AAR in evaluating the magnitude of age mixing within Holocene assemblages.

AAR data for the coastal plain of Argentina between ~35°S and ~55° S for multiple taxa identify both Holocene and Pleistocene aminozones (Rutter et al. 1989, 1990; Aguirre et al. 1995). Two Pleistocene aminozones are recognized, one representing at least a portion of the last interglacial high sea stand. Electron spin resonance (ESR) provides limited independent calibration. Last interglacial shoreline deposits are usually found between 10 and 15 m above sea level. AAR data indicate that some deposits, at elevations up to ~40 m, are older than the last interglacial. Holocene coastal/marine deposits are also found in this region, at elevations up to ~5 m, so there is ample potential for age mixing.

Carr et al. (2010) reported AAR data for marine mollusks and terrestrial gastropods from sites along the coast of South Africa. Optically stimulated luminescence (OSL) results provided the primary age control, indicating formation of beach deposits and associated dunes between 138 ± 7 ka and 113 ± 6 ka, at elevations up to ~8 m above sea level. AAR data, while limited, are consistent with these age estimates.

AAR Studies of Submerged Deposits, Continental Margins

AAR data for shallow submerged portions of the continental margins of Europe, Australia, North America, and Antarctica also exist. In many cases, these studies compare offshore data with results from nearby onshore sites. Along the US Atlantic margin, aminozones representing multiple intervals of deposition during the Pleistocene are encountered from offshore New Jersey, Maryland, Delaware, and North Carolina (Toscano and York 1992; Groot et al. 1995; Wehmiller et al. 2010; Miller et al. 2013). In most cases there are associated lithostratigraphic, paleontological, and geophysical data to aid in the environmental analysis of the AAR data. Sr-isotope age estimates

provide some qualitative calibration for some of the older (early Pleistocene) aminozones (Wehmiller et al. 2012; Miller et al. 2013). These continental margin records usually contain evidence of multiple transgressive-regressive cycles associated with sea-level changes during the Pleistocene, as in the case of southeastern Australia (Murray-Wallace et al. 2005), the North Sea (Meijer and Cleveringa 2009), and the Black Sea (Nicholas et al. 2011). AAR results from deeper water environments off northeastern Australia (Hearty et al. 2004) demonstrate the kinetic effects of different bottom water temperatures (see ► [Marine Sediments](#)).

Low-Latitude Carbonate Islands and Reefs

The stratigraphy and geochronology of deposits on numerous low-latitude islands from the Atlantic and Pacific Oceans have been studied using AAR, using either land snails, whole-rock analyses of carbonate eolianites (see ► [Eolianites](#)), or marine mollusks. In many cases the results contribute to the chronology of local eolianite (dune) formation, usually associated with local relative sea-level histories. Studies of Pleistocene units from Atlantic, Mediterranean, or Caribbean islands include Bermuda (Hearty et al. 1992, 2007), the Bahamas (Hearty and Kaufman 2000; Hearty 2010), Jamaica (Goodfriend and Mitterer 1993), Barbados (corals) (Wehmiller et al. 1976), Madeira (Goodfriend et al. 1996a), the Canary Islands (Zazo et al. 2002), and the Mediterranean region (Hearty et al. 1986; Hearty 1987; Rose et al. 1999). Pacific Island studies include Lord Howe Island (Brooke et al. 2003; Woodroffe et al. 2006), New Guinea (Hearty and Aharon 1988), and Hawaii (Hearty et al. 2000, 2007). AAR studies of Holocene corals from assorted localities establish the kinetics of racemization during the earliest phases of diagenesis (Hearty and Aharon 1988; Goodfriend et al. 1992; Hendy et al. 2012; Tomiak et al. 2013). The tropical temperatures at which these corals are found enhance the overall rate of racemization, allowing high-resolution kinetic studies.

Coastal Regions Influenced by Glaciations

Discussions of these regions will be found in separate entries (► [Arctic Environment](#), [Loess and Glacial](#)), but selected references for these areas are reviewed here (see Fig. 1).

High-latitude coastal regions that have been affected by glaciations reveal a complex record of Quaternary deposition. AAR-dated samples are often transported from their original site of deposition, but results from these samples can constrain histories of ice dynamics and local relative sea-level history. Along the Arctic margins of Pleistocene ice sheets, ice margin and sea-level histories are documented in northeastern Siberia, northwest Alaska, Baffin Island, Greenland, and Spitzbergen (Miller et al. 1992; Kaufman 1992; Kaufman and Brigham-Grette 1993; Funder et al. 1994; Brigham-Grette and Hopkins 1995; Goodfriend et al. 1996b; Kelly et al. 1999; Brigham-Grette et al. 2001; Gualtieri et al. 2003; Mangerud et al. 2008; Refsnider et al. 2013).

Along the southern margin of the Laurentide Ice Sheet, clusters of D/L values in mollusks identified multiple advances of ice in the Hudson Bay Lowland, including events that were recognizable only in transported samples found in glacial sediments (Andrews et al. 1983; Thorleifson et al. 1992). AAR data for in-place estuarine mollusks identified both pre- and post-last glacial fossiliferous deposits in the St. Lawrence valley (southeastern Canada) using AAR analyses of marine mollusks (Occhietti et al. 1996).

A long history of AAR study of sites along the southern margin of the Scandinavian Ice Sheet and associated sites in the United Kingdom exists. Miller and Mangerud (1985) and Sejrup et al. (2000) analyzed AAR in mollusks found in marine and glacial deposits of the North Sea, Norway, Denmark, Germany, and the Netherlands. Meijer and Cleveringa (2009) summarized AAR data for the region, generated by several laboratories over three decades. Bowen (2000) and Penkman et al. (2011, 2013) used AAR data to interpret the glacial, marine, and nonmarine records of the United Kingdom. Almost all of these studies demonstrate that multiple phases of deposition, either shallow marine or fluvial, are apparent in the regional record, extended back through the entire Pleistocene.

Application of AAR to high-latitude Southern hemisphere sites includes southern Chile (Clapperton et al. 1995) and Antarctica (Hart and Webb 1998; Forsberg et al. 2003; Gardner et al. 2006). Each of these studies includes AAR and other independent chronological information to reconstruct local histories of glacial advance and retreat. As with other high-latitude studies, the low temperatures of these regions result in very slow racemization kinetics, meaning that low D/L values are observed even in samples that are perhaps as old as 4 Ma.

Summary and Conclusions

The use of racemization in the study of Quaternary coastal environments and processes has a history almost as long as the history of the AAR dating method itself, as some of the earliest studies involved fossils from coastal sites along the US Atlantic coast (see Wehmiller 2013, for review). Regions of study range from polar to equatorial latitudes, with potential age ranges for application being determined by the effective temperatures in these climates. Many coastal studies, in particular, benefit from associated U–Th dating of associated corals (at low- or mid-latitude sites), the preferred sample type for U-series dating. In addition, AAR data from coastal studies have yielded important insights into geochemical and taxonomic factors that influence racemization, particularly in situations where long relative age sequences of samples are available. Extensive AAR study of major active continental margins includes marine terraces on the Pacific coasts of North and South America and the Mediterranean; passive continental margins include the Atlantic coasts of North and South America and much of the coast of Australia, including several long chronologic sections spanning the entire Quaternary. Studies of sites in high northern latitude regions in North America (Baffin Island) and Europe (United Kingdom, Scandinavia, and the southern North Sea) have been historically important for the development of AAR methods and have contributed substantial insights into the Quaternary glacial and climate history of northern hemisphere ice sheets. Data from lower-latitude sites provide a broad perspective for comparison with mid- and high-latitude results, and a large dataset exists for a variety of types of carbonate (marine and eolian) deposits on tropical islands from the Atlantic, Pacific, and Mediterranean. These latter results come from a variety of sample types not usually sampled from higher-latitude sites, and the rapid racemization at low-latitude temperatures permits high-resolution kinetic and age-mixing studies.

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Volcanic Glass (Fission Track)

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Definition

Volcanic glass. An amorphous, noncrystalline solid produced by the rapid cooling of magma during a volcanic eruption.

Fission track in glass. An etched conical pit formed by the preferential solution of glass along a latent fission track, which, in turn, is formed by the spontaneous fission of ^{238}U or induced fission of ^{235}U .

General Considerations

Fission-track (FT) dating methods provide meaningful ages using silicic volcanic glass and are particularly applicable to the dating of young volcanics in calc-alkaline terrains where the $^{40}\text{Ar}/^{39}\text{Ar}$ method is less suitable due to low potassium values. Successful glass–FT ages have been obtained on tephra beds as young as Late Pleistocene and as old as Middle Eocene, as demonstrated herein, and the ability to date very fine-grained, typically contaminated, distal tephra has been an important boost to the geochronology of regions distant from volcanic centers – in both terrestrial and marine environments.

Fission tracks in glass are revealed by etching in hydrofluoric acid. They are conical pits due to the isotropic properties of glass and a track etch rate that is not much greater than the bulk etch rate. Shapes, as seen under an optical microscope, vary from circular to elliptical, depending on the orientation of the axis of the cone with respect to the polished surface (Fig. 1).

Volcanic glass must meet several conditions before meaningful FT dates can be determined (Faure 1977). The U concentration must be sufficient to give a statistically significant age. Tracks must be stable at ambient temperatures, true of glass, but partial fading of fission tracks (PTF) occurs in all glasses, and correction procedures must be applied to account for this condition. The glass should be free of microlites and other inclusions, which, upon etching, can resemble fission tracks. Furthermore, the glass surface area must be large enough to permit accurate measurement of the areal FT densities. Obsidian typically meets these criteria (Bigazzi and Bonadonna 1973; Doriguel et al. 1998), but glass shards in some tephra beds do not. Bubble-wall glass shards can be readily dated (Fig. 2a), but not pumiceous pyroclasts (Fig. 2b). The lower limit in grain size is $\sim 80\text{ }\mu\text{m}$. Uranium must be distributed uniformly throughout the glass, a requirement that can be assessed directly by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Pearce et al. 2004). The glass must be unaltered, and, in the case of tephra beds, the shards must

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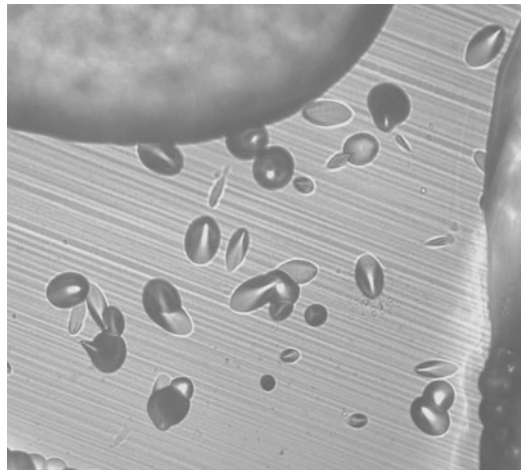


Fig. 1 Induced fission tracks in a glass shard of Huckleberry Ridge Tuff, Kansas, USA (UT1366), as seen using an optical microscope. Parallel lines across glass shard are polishing scratches, purposely made to indicate the internal surface. The mean track diameter is $8.38 \pm 0.10 \mu\text{m}$

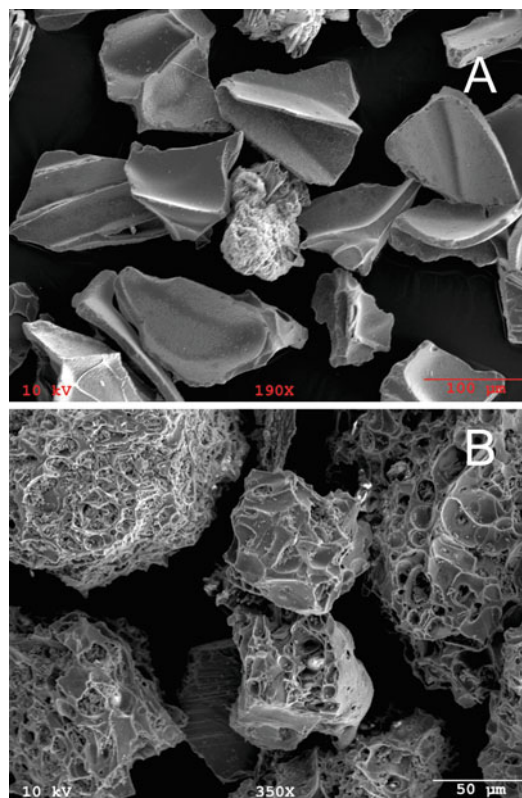


Fig. 2 (a) Bubble-wall glass shards of the late Pleistocene Youngest Toba Tuff (YTT), Indonesia, and (b) pumiceous pyroclasts from the late Pleistocene Sheep Creek tephra, Yukon, Canada. The latter tephra bed cannot be dated by glass–FT methods because of insufficient glass surface area, but tephra beds with glass shards similar to those of YTT are readily dated by fission tracks

belong to a single population; tephra beds with multiple glass populations, primary or reworked from earlier tephra deposits, do not provide meaningful FT dates. A unimodal glass population should be demonstrated by major- and trace-element analyses prior to FT dating. Contamination of

the sample by mineral grains, however, does not compromise the date because glass–FT methods are grain specific in the sense that the track data are gathered by examination of individual glass shards in each field of view under the microscope so that mineral grains can be readily recognized and ignored. The sample must not have been exposed to any post-depositional heating that would cause resetting of its fission tracks – a condition that could occur in geothermal areas or where tephra beds have been affected by high temperatures associated with emplacement of younger igneous bodies. As with all geochronologic studies, the stratigraphic and sedimentologic contexts of the deposit must be well established.

Silicic, hydrated glass shards of low vesicularity are ideal for FT dating. They are the most abundant phase of tephra beds; they are mostly homogeneous and rarely contain microlites or inclusions; they have uniform etching characteristics; and U contents typically range from 2 to 8 ppm for rhyolitic to dacitic glasses, enough to give statistically viable ages for tephra beds as young as Late Quaternary (Alloway et al. 2004a). Under conditions of rapid cooling during the eruption and storage at near-surface temperatures, geologically meaningful formation ages can be obtained. In addition, because fine-grained shards can be dated by glass–FT methods, the geochronology of regions far from volcanic centers can be tackled due to the common widespread distribution of silicic tephra beds (Westgate et al. 2007). One of the earliest successful examples of glass–FT dating involved the use of glass shards to determine the age of Bed 1 at Olduvai Gorge (Fleischer et al. 1965a, 1975). The FT age of 2.0 ± 0.3 Ma agreed with the K–Ar age of 1.75 ± 0.05 Ma, obtained earlier by Leakey et al. (1961).

Another important consideration in FT dating is the suitability of a glass standard. Although the Moldavite tektite is the formal glass age standard (IUGS Commission on Geochronology; Hurford 1990; Balestrieri et al. 1998), its practical use is limited by the requirement that all splits for distribution to FT laboratories must come from one single sample. Necessary attributes of an age standard are that it contains sufficient tracks to give a statistically meaningful age and that no PTF has occurred. It is doubtful that such a glass exists, especially hydrated glass, but the closest contender is the Jankov Moldavite. Other recommended age standards are Roccastrada R2V, macusanite, and the Japanese glass JAS-G1 (Balestrieri et al. 1998). The University of Toronto FT laboratory currently uses the Huckleberry Ridge tephra from Meade County, Kansas, USA, to monitor accuracy of its FT age determinations. This tephra bed has large glass shards with no mineral inclusions, high U content (~ 8 ppm), a reference $^{40}\text{Ar}/^{39}\text{Ar}$ age of 2.003 ± 0.014 Ma (2σ ; Gansecki et al. 1998), and abundant spontaneous fission tracks, making it a useful informal reference glass. PTF has occurred ($D_s/D_i = 0.81 \pm 0.02$ based on six samples; D_s is the mean diameter of spontaneous tracks and D_i is the mean diameter of induced tracks), but well-established correction procedures are available (see below).

Glass–FT Dating Methods

The most commonly used FT dating method is the zeta calibration method based on analysis of age standards (Hurford and Green 1983), which, in the case of glass–FT dating, is the Moldavite tektite with an age of 14.34 ± 0.08 Ma (Laurenzi et al. 2003, 2007). An age can be determined by measuring three areal track densities, spontaneous track density (ρ_s), induced track density (ρ_i), and induced track density of the dosimeter glass (ρ_d) or its muscovite external detector. The area is determined using an eyepiece graticule when the glass surface area is large, such as with obsidian and proximal tephra samples. Smaller glass shards require use of the point-counting technique

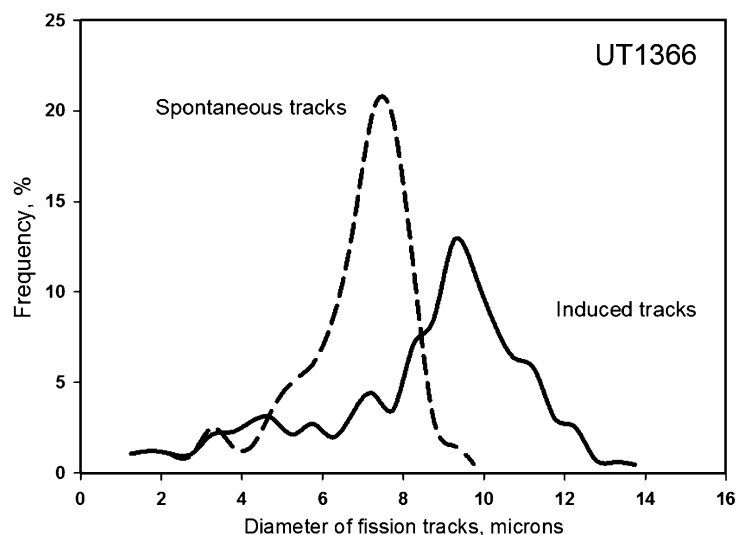


Fig. 3 Size frequency curves of FT diameters in glass shards of Huckleberry Ridge Tuff demonstrating partial track fading – the spontaneous tracks are much smaller than the induced. The mean diameter of spontaneous tracks is $6.85 \pm 0.10 \mu\text{m}$ ($n = 200$) compared to $8.38 \pm 0.10 \mu\text{m}$ ($n = 663$) for the induced tracks

(Naeser et al. 1982), in which case, an additional experimental error is involved (Bigazzi and Galbraith 1999).

Determination of ρ_s and ρ_i can be done in one of two ways: the population and population-subtraction methods (Wagner and Van den Haute 1992). In the former, the sample is split into two aliquots, one of which is heated to remove the spontaneous tracks, irradiated, and then used to obtain ρ_i . The spontaneous track density, ρ_s , is obtained from the unheated aliquot. Whereas this method is acceptable for obsidian, it is not good for hydrated glass shards. The differential heat treatment means that track-etching efficiencies for ρ_s and ρ_i are different and heating above 200°C drives off water and produces brittle glass shards which readily fracture when polished, reducing the glass surface area when etched. Surfaces with a network of fine fractures are also produced, hindering track recognition (Naeser et al. 1980). A better and recommended approach does not use any heat treatment. The induced track density, ρ_i , is calculated by determining the areal track density of the irradiated aliquot and then subtracting ρ_s .

Correction Methods for PTF in Glasses

Temperature is the dominant factor influencing the stability of latent fission tracks in natural glasses (Fleischer et al. 1965b). With progressive heating, latent tracks shorten and result in a reduced areal track density, giving an age that is too young. Even at ambient surface temperatures, PTF takes place (Naeser et al. 1980). Therefore, all glass-FT ages must be corrected for PTF. An example of a tephra bed (Huckleberry Ridge Tuff, UT1366) that has experienced PTF is shown in Fig. 3. The spontaneous fission tracks are distinctly smaller than the induced tracks.

Several procedures have been developed to correct for PTF (Arias et al. 1981; Storzer and Wagner 1969). Two are mentioned here. Experimental studies by Sandhu and Westgate (1995) demonstrated a near 1:1 relationship between ρ/ρ_o and D/D_o , where ρ_o and D_o are the original areal track density and mean track diameter, respectively. If the sample is etched to give $D_o (= D_i)$ in the range of 6–8 μm , the corrected spontaneous areal track density (ρ_{sc}) is given by

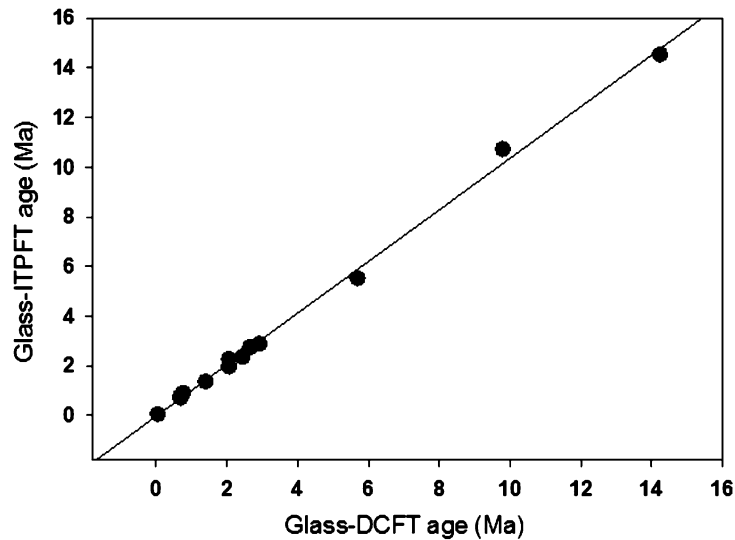


Fig. 4 Close correspondence between glass–DCFT and glass–ITPFT ages demonstrating a near 1:1 relationship. The regression line has $r^2 = 0.997$. See Table 1 for further details

$$\rho_{sc} \approx \rho_s \left(\frac{D_i}{D_s} \right) \quad (1)$$

Of the many tephra samples we have dated by this diameter-corrected FT method (DCFT), D_i/D_s values range from 1.10 (75 ka) to 1.41 (2 Ma), but there is no correlation between age and magnitude of this correction. The mean value of D_i/D_s is 1.22 ± 0.08 .

The isothermal plateau FT (ITPFT) method uses a single heat treatment of 150 °C for 30 days to correct fully for PTF (Westgate 1989). The FT age of a sample is proportional to ρ_s/ρ_i , and the point at which this ratio does not change with increasing time at a specified temperature – the plateau condition – signals a full correction for PTF and is confirmed by $D_s = D_i$. Kitada and Wadatsumi (1995b) showed that increasing the temperature to 165 °C for 5 days was enough to give a plateau age. Other time-temperature conditions used to correct for PTF are given in Westgate et al. (2007) with a cautionary note to the effect that plateau-annealing conditions should be such as to minimize structural damage to the glass because of potential negative effects on its etching characteristics – a long time–low temperature combination being favored.

Comparison Between Glass–FT Dating Methods

A comparison between glass–DCFT and glass–ITPFT ages is shown in Fig. 4 and Table 1. Good agreement exists and adds confidence to the validity of both methods. The heat treatment required in the ITPFT method increases the thermal stability of fission tracks so that an adequate etch requires a longer time compared to that required in the DCFT approach. As a result, the lower size limit of glass shards to be dated by the ITPFT method is $\geq 120 \mu\text{m}$ whereas shards as small as $\sim 80 \mu\text{m}$ can be dated by the DCFT method.

Accuracy and precision of glass–FT ages can be gleaned from Table 2. Ages range from 48 ka to 38 Ma and all are within $\sim 10\%$ of the mean age determined by other methods, mostly $^{40}\text{Ar}/^{39}\text{Ar}$ ages. Furthermore, all glass–FT ages agree with those ages derived by other methods at the 1σ criterion, with the exception of the Cindery Tuff. In particular, excellent agreement exists with the

Table 1 Comparison of glass–DCFT and glass–ITPFT ages

Sample name	Glass–DCFT age	Glass–ITPFT age	References
Huckleberry Ridge Tuff (UT1366)	2.06 ± 0.17	1.97 ± 0.22	This entry
North Birch Creek tephra (UT2273)	9.80 ± 0.56	10.73 ± 0.96	This entry
BT-28 (UT1395)	5.69 ± 0.53	5.52 ± 0.18	Westgate et al. (2011)
Hollis tephra (UT2207)	690 ± 45 ka	695 ± 35 ka	Preece et al. (2011)
Gold Run tephra (UT1907)	669 ± 64 ka	735 ± 88 ka	Westgate et al. (2009)
UT1786 (Idaho, USA)	2.92 ± 0.29	2.88 ± 0.34	This entry
Opoli tephra (UT1655, 1657)	2.06 ± 0.18	2.27 ± 0.26	Roberts et al. (2007)
Roccastrada R2V glass (UT1545)	2.44 ± 0.09	2.36 ± 0.10	Balestrieri et al. (1998)
Jankov Moldavite (UT1546)	14.24 ± 0.44	14.54 ± 0.49	Balestrieri et al. (1998)
Mozume Ash (UT1620), Japan	757 ± 79 ka	899 ± 109 ka	This entry
Lost Chicken tephra (UA771, UT86)	2.66 ± 0.17	2.75 ± 0.41	Matthews et al. (2003)
Maninjau Ignimbrite (UT1418)	48 ± 6 ka	48 ± 6 ka	Alloway et al. (2004a)
Fort Selkirk tephra (UT82)	1.40 ± 0.13	1.36 ± 0.24	Westgate et al. (2001)
Giraffe tephra (UT2114, 2115)	37.42 ± 3.55	39.37 ± 3.53	Doria et al. (2011)

The population–subtraction method was used. Ages calculated using the zeta approach and $\lambda_D = 1.551 \times 10^{-10}$ year⁻¹. Zeta value is 301 ± 3 based on six irradiations at McMaster Nuclear Reactor, Hamilton, Ontario, using the NIST SRM 612 glass dosimeter and the Moldavite tektite glass (Lhenice locality) with an ⁴⁰Ar/³⁹Ar age of 14.34 ± 0.08 Ma (Laurenzi et al. 2003, 2007). Ages in Ma unless otherwise noted; 1σ given

⁴⁰Ar/³⁹Ar ages on the reference glasses, Jankov Moldavite, Roccastrada R2V glass and JAS-G1 obsidian (Balestrieri et al. 1998), as well as the Huckleberry Ridge Tuff.

Precision is within 10 % for the reference glasses but is ~15 % for the other tephra beds. Values are better when an eyepiece graticule can be used to determine area as opposed to the point-counting technique. Precision can be improved if DCFT and ITPFT ages are determined on a given tephra bed and a weighted mean age and associated error calculated using the standard inverse variance method (Bevington 1969). For example, the age of Giraffe tephra given in Table 2 is a weighted mean age and associated error of the two age determinations listed in Table 1.

Summary and Conclusions

Fission tracks are stable in glasses, as shown by their presence in silicic tephra beds of Middle Eocene age, but, over time, they suffer from PTF, even at ambient surface temperature conditions. As a result, a correction for ρ_s must be applied in order to obtain accurate FT ages. Several correction procedures have been developed; some are based on FT size data (e.g., DCFT method), others involve heat treatment (e.g., ITPFT method). Obsidian and glass shards of silicic tephra beds are the most common types of volcanic glass used in FT dating studies. Accuracy is within ~10 % of the age determined by other methods, mostly ⁴⁰Ar/³⁹Ar ages, and precision is in the range of 10–15 %. Both are acceptable. A limiting factor in attainment of good precision is the glass surface area available for counting fission tracks. This is usually not a problem with obsidians but is very relevant to glass shards of distal tephra beds. Introduction of the point-counting technique to estimate ρ_s and ρ_i has greatly helped in this regard. Acceptable ages can now be obtained on glass shards as small as ~80 μm. It follows, therefore, that these grain-specific FT methods are ideally suited to the dating of distal tephra beds, which are typically thin, discontinuous, fine-grained, and

Table 2 Accuracy and precision of glass fission-track ages: a comparison with other dating methods

Sample	Glass type	Glass–FT age (Ma) ($\pm 1\sigma$)	Age using other dating methods (Ma)	References
Jankov Moldavite (Czech R.)	Tektite	14.24 ± 0.44	14.34 ± 0.08	Laurenzi et al. (2003, 2007)
Roccastrada R2V (Italy)	Glass shards	2.44 ± 0.09	2.36 ± 0.10	Bigazzi et al. (1993)
JAS-G1 (Japan)	Obsidian	0.93 ± 0.06	0.95 ± 0.005	Kitada and Wadatsumi (1995a)
Huckleberry Ridge Tuff (USA)	Glass shards	2.06 ± 0.17	2.003 ± 0.014	Gansecki et al. (1998)
Potaka tephra (New Zealand)	Glass shards	0.93 ± 0.14	1.00 ± 0.03	Alloway et al. (2004a)
Ongatiti Ignimbrite (New Zealand)	Glass shards	1.08 ± 0.12	1.21 ± 0.04	Alloway et al. (2004b)
Maninjau Ignimbrite (Indonesia)	Glass shards	48 ± 6 ka	53 ± 2 ka	Alloway et al. (2004a)
Lake Tapps tephra (USA)	Glass shards	1.00 ± 0.16	1.15 ± 0.01	Hildreth (1996)
Rangitawa tephra (New Zealand)	Glass shards	0.30 ± 0.05	$0.35 \pm 0.01^*$	Pillans et al. (1996)
Mamaku Ignimbrite (New Zealand)	Glass shards	0.21 ± 0.03	0.22 ± 0.01	Houghton et al. (1995)
Ash a1 (Crotone series, Italy)	Glass shards	2.31 ± 0.34	2.31^*	Suc et al. (2010)
BKT-3 tephra (Ethiopia)	Glass shards	1.94 ± 0.37	2.3^*	Hart et al. (1992)
SHT tephra (Ethiopia)	Glass shards	3.35 ± 0.35	3.40 ± 0.03	Walter and Aronson (1993)
Moiti tephra (Ethiopia)	Glass shards	3.68 ± 0.51	4.1^*	Hart et al. (1992)
Cindery Tuff (Ethiopia)	Glass shards	3.50 ± 0.32	3.94 ± 0.05	Hall et al. (1984)
Fort Selkirk tephra (Canada)	Glass shards	1.36 ± 0.24	$>1.47 \pm 0.11^*$ $<1.60 \pm 0.08^*$	Westgate et al. (2001)
Old Crow tephra (Canada)	Glass shards	124 ± 10 ka	$>128 \pm 22$ ka* $<144 \pm 22$ ka*	Berger et al. (1996)
Quartz Creek tephra (Canada)	Glass shards	2.82 ± 0.23	2.64 ± 0.24 $>2.71 \leq 3.01$	Westgate et al. (2003)
Giraffe tephra (Canada)	Glass shards	38.40 ± 2.50	Middle Eocene plants	Doria et al. (2011)

Analytical information on glass–FT ages is given in Table 1. Other ages determined by the $^{40}\text{Ar}/^{39}\text{Ar}$ method unless noted with an asterisk: Rangitawa tephra and Ash a1 by orbital tuning, Moiti tephra and Fort Selkirk tephra beds by K/Ar, Old Crow tephra by thermoluminescence, and BKT-3 tephra by zircon–FT method

contaminated. They will greatly facilitate development of detailed tephrostratigraphic frameworks far from volcanic centers – in both terrestrial and marine environments.

Cross-References

- [Fission Track Dating](#)
- [Tektites](#)
- [Tephrochronology](#)

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Uranium-Lead, Detrital Zircon

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Synonyms

[Detrital zircon analysis](#), [Zircon provenance](#)

Definitions

Detrital zircon: The mineral zircon (ZrSiO_4) is a common accessory mineral of many felsic igneous rocks. Because of its high relative hardness and chemical inertness, zircon mineral grains in a source rock can survive weathering and erosion to produce detrital grains that are transported to sedimentary deposition.

Uranium-lead radiometric dating: Some minerals, such as zircon, incorporate trace amounts of uranium in their crystal lattice when they form from a melt. The two principal isotopes of uranium (^{238}U and ^{235}U) are unstable and decay to form stable isotopes of lead (^{206}Pb and ^{207}Pb) over hundreds of millions of years. The rate of decay is known and measuring these isotopes in a sample allows the age of mineral formation to be calculated.

Sedimentary provenance: Sedimentary rocks are composed of detrital minerals derived from previously existing rocks. Some of these detrital minerals, for example, zircon (ZrSiO_4), preserve characteristics such as chemistry or radiometric age that can help identify the original rock source, or protosource, of those minerals when compared with data from previously analyzed rocks. In some cases, the detrital grains may be the only remaining evidence of the original rock. Integrating protosource information with other information such as petrology, paleogeographic reconstructions, and other detrital zircon data can build interpretations on the history, or provenance, of sedimentary detritus from protosource to final deposition.

Introduction

Sedimentary rocks are records of surface conditions and processes during Earth's history. Along with bulk physical features and chemical properties, the composition of the detrital mineral grains in sedimentary rocks has long been recognized as important information in understanding the origin and depositional processes of that sedimentary rock – information that can build interpretations about ancient environments and the ancient location of mountain belts and continents.

Descriptive studies and provenance interpretations of sedimentary rocks have traditionally focused on the heavy mineral or accessory phases as having characteristics that are considered diagnostic of origins, environments, and tectonic settings (e.g., Rittenhouse 1943; Morton and Hallsworth 1994). Zircon (ZrSiO_4) is especially useful because of a common distribution in most sedimentary rocks and its retention of chemical and isotopic features through most geological

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processes to the point of melting. The robustness of the uranium-lead (U-Pb) radiometric system in zircon has been particularly useful, as an age of a mineral grain is a proxy for the source rock where it formed.

The techniques to measure the U-Pb age of detrital zircon have developed considerably in the last 50 years to where techniques are relatively inexpensive, rapid, and widely applied. Applications typically include the development of regional, and sometimes global, provenance and evolution models with a highlight being the discovery of the oldest terrestrial materials that provide a unique window into the early Earth. Recent studies are increasingly focused on refining the interpretation of those models with the integration of other analytical techniques or detailed study of modern analogues in order to test assumptions and understand potential biases.

Historical Development of Analytical Methods

The development of detrital zircon geochronology parallels, and in some cases has driven, the broader development of isotopic analytical equipment and methods (see Gehrels [2012](#), Ireland [2013](#), Nemchin et al. [2013](#), and the references therein for more descriptions of analytical methods and their development). The emergence of mass spectrometry equipment for applied geoscience research in the 1960s saw initial multigrain studies of detrital zircons as a reconnaissance tool in North American geology, e.g., Ledent et al. ([1964](#)) and Houston and Murphy ([1965](#)).

As equipment and methods developed through the 1970s and 1980s, analysis of single grains or even parts of single grains became possible with increasing precision initially via the labor-intensive chemical treatment of isotope dilution thermal ionization mass spectrometry (ID-TIMS) methods (e.g., Ross and Parrish [1991](#); Gehrels et al. [1995](#)). The emergence of secondary ionization mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analytical equipment in the 1980s and 1990s revolutionized detrital zircon geochronology with rapid in situ analysis of small portions of individual grains.

The increasing speed of data collection also enables the collection of larger, statistically valid, datasets. The power of the in situ techniques was illustrated early in their development with the discovery of Hadean detrital zircon from Archean-aged metasedimentary rocks at Mt. Narryer in Western Australia (Froude et al. [1983](#)) and nearby Jack Hills (Compston and Pidgeon [1986](#)) using a Sensitive High Resolution Ion Microprobe (SHRIMP). In these samples, Hadean-aged grains may only form a few percent of the total detrital zircon population (which itself was typically <0.1 % of the total rock). The larger number of single-grain analyses possible with the in situ technique meant that it was more likely to find such rare occurrences.

Detrital zircon geochronology applications and techniques have expanded rapidly in the first decade of the twenty-first century, particularly with improvements in LA-ICP-MS equipment such as multi-collectors and technique refinements including measurement of common Pb (see Košler et al. [2002](#); Gehrels et al. [2006](#), [2008](#); Frei and Gerdes [2009](#) for further details of methodology development). Although solutions for the remaining issues around standardizing data acquisition, processing, and reporting are still being pursued (Horstwood [2008](#)), hundreds of papers based on detrital zircon geochronology are published every year.

Biases and Validity, Statistics and Interpretation

Detrital zircon geochronology is founded on the assumption that analyzed samples are representative of the protosource and that large datasets provide statistically valid quantitative information on proportions that accurately reflect the mass balance of detritus through the “sediment factory” (von Eynatten and Dunkl 2012). In reality, there are many potential natural and artificial biases that need consideration (Fedó et al. 2003).

The first set of natural biases relate to the origin of zircon itself. Zircon is preferentially formed in felsic igneous rocks so mafic protosources will be naturally underrepresented in zircon-based provenance analysis. Furthermore, whole regions may have marked enrichment in zircon content which, given the robust nature of the mineral, can dominate subsequent sedimentary units for aeons. For example, zircons from the granites emplaced during the Grenville Orogeny in eastern Laurentia around 1,150–1,050 Ma have been a dominant mode in subsequent Appalachian sedimentary history despite complex accretion tectonics through the Paleozoic (Moecher and Samson 2006).

A second set of natural biases occur with the sedimentological processes of weathering, transport, and deposition. Detrital zircon is assumed to have the same provenance as quartz and feldspar grains that form the bulk of a sedimentary rock although it is well known that denser zircon grains have higher settling velocities in a transporting fluid (Garzanti et al. 2008, 2009). Lawrence et al. (2011) demonstrate modern hydrodynamic fractionation within the zircon fraction using five samples taken from different locations on the same dune bedform in the Amazon River with significant difference in the proportions of age components (Fig. 1). Correlations between age and grain size of detrital zircons have also been shown in ancient sedimentary units (e.g., Gehrels et al. 1996; Sircombe et al. 2001).

Several studies have specifically targeted modern fluvial sedimentary deposits to illustrate potential biases against true proportionality. Cawood et al. (2003) and Sláma and Košler (2012)

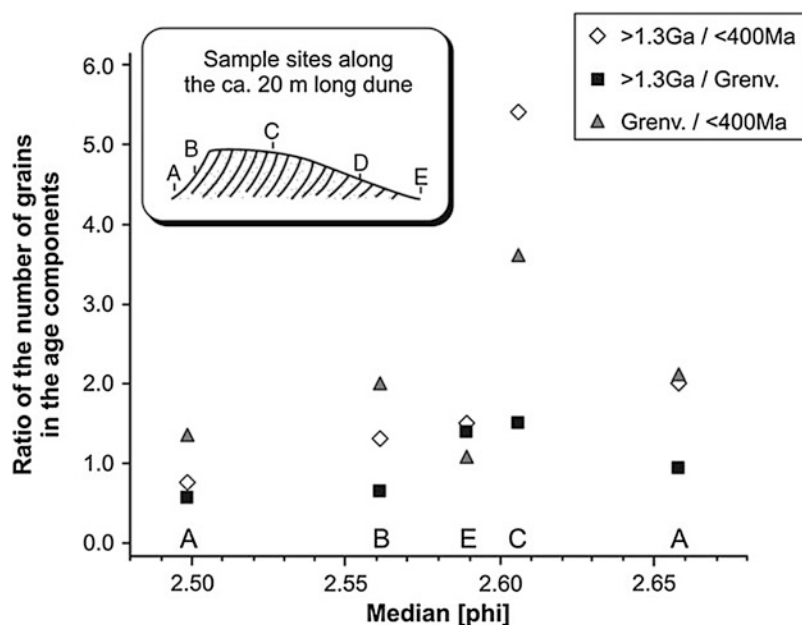


Fig. 1 Variation in ratios of detrital zircon U-Pb age groups against grain size (phi) from a single dune bedform in the lower reaches of the Amazon River. *Diamonds* show ratio of ages >1,300 Ma against ages younger than 400 Ma, *squares* show ages >1,300 Ma against Grenvillian ages, and *triangles* show Grenvillian ages against ages younger than 400 Ma (Figure from von Eynatten and Dunkl (2012), based on Lawrence et al. (2011))

examined a series of detrital zircon samples from rivers in southern Western Australia and Scotland respectively that crossed major geological boundaries to illustrate the persistence of zircon sourced in the upper catchments. Whole catchment studies in central Nepal (Amidon et al. 2005) and in the Colombian foreland (Saylor et al. 2013) indicate that proportions of detrital zircon in modern fluvial sediments accurately represent the current exposure of potential protosources and their relative zircon fertilities. In comparison, a study of detrital zircon in the major tributaries of the Indus River, Pakistan, indicates less certain direct pathways between current exposure of bedrock and zircon age components in modern fluvial sediments (Alizai et al. 2011). Intriguingly, differences are attributed to temporal changes in the catchment regions such as intensity of monsoon rain linked with erosion rates with an estimated transport time of 5–10 ka.

DeGraaf-Surpless et al. (2003) in the Methow Basin in northern Washington and southern British Columbia and Smith and Gehrels (1994) in the Roberts Mountains allochthon, Nevada, demonstrate correlations between sedimentary maturity or lithofacies and expected age distribution. More mature sediments such as arenites generally contain the broader range of zircon age components, but closely spaced samples are relatively similar. Conversely, more immature sediments such as fluvial sandstones contain narrower ranges of zircon age components, but related samples are more dissimilar. These results indicate that more samples need to be collected for immature sediments to represent possible provenances.

Sample Preparation

Sample processing and mineral separation methods are a potential source for artificial biasing of a detrital zircon sample.

Rock crushing and milling is the typical first step for indurated sedimentary rocks. Early studies in granites suggest that there is little or no biasing of zircon caused by simple mechanical crushing (Larsen and Poldervaart 1957). However, more recent work (Hay and Dempster 2009) indicates substantial loss of any low-temperature or altered zircon present.

Density separation is a common second stage of sample preparation using water flow in a Wilfley concentration table (Niebur and Fell 1982), elutriation tubes (Frost 1959; Van der Westhuizen et al. 1993), or settling rates in various heavy liquids (Krumbein and Pettijohn 1938; Callahan 1987). Sláma and Košler (2012) explicitly tested for preferential loss of the small-grain fractions in a synthetic detrital zircon sample using Wilfley table and heavy liquid processes. They demonstrate that the Wilfley table process itself did not cause preferential loss, although heavy liquid separation alone did, possibly due to any electrostatic buildup during handling of the sample more likely to affect the smaller grains.

The typical third stage of zircon separation uses Frantz magnetic barrier separators to differentiate zircon based on magnetic susceptibility and the correlation between concordance and low or negative magnetic susceptibility (Silver 1963). Using a sample with a bimodal age distribution, Sircombe and Stern (2002) demonstrated the potential for biasing a detrital zircon age distribution in various magnetic fractions.

The final stage of sample preparation involves manual manipulation to mount individual zircon grains for analysis. Moecher and Samson (2006) discuss the biases that may occur with the often inadvertent preference for larger grains that are easier to manipulate and sufficiently large for in situ analysis. Preference for larger grain sizes is also demonstrated in interlaboratory calibration tests (Košler et al. 2013). Unless smaller grains are deliberately targeted, typical grain sizes >100 µm are chosen to accommodate ablation pits of 20–50 µm diameter.

Cathodoluminescence imaging of sectioned zircon is vital to understand the evolution of single grains and better interpret the resulting analyses (Hanchar and Miller 1993). Although the volume of

detrital zircon samples may make this process more laborious, the need for this level of understanding is also critical in provenance studies and provides extra dimensions to the age data (Hietpas et al. 2011).

Analytical Protocols

The protocol for analyzing detrital zircon samples has a profound effect on how the acquired data should be interpreted, and there are two principal strategies (Fedo et al. 2003).

The first strategy is “qualitative” where data are sought from every component in the population, typically guided by color, morphology, and internal structure (e.g., Gehrels and Dickinson 1995; Åhäll et al. 1998). This approach reduces the chance of missing a provenance component (Gehrels 2000) although it means data may be unsuitable for subsequent statistical comparison with other samples (Sircombe and Hazelton 2004).

The second strategy is a “quantitative” approach where a large number of grains are analyzed in an attempt to represent the true proportions in the population. At least 59 randomly selected grains need to be analyzed to reduce the probability of missing 1 in 20 components to 5 % (Dodson et al. 1988). This value was widely used; however, the formula has been reevaluated (it had been originally intended to describe searching for the *oldest* component, not all possible components), and the number of analyzed grains required to reach the same level of confidence should be 117 (Vermeesch 2004). However, this is the worst-case scenario that assumes randomly selecting grains from a uniform distribution of potential ages across all geological time. There are some experiments on natural and synthetic samples that suggest that >100 analyses are not required to reliably detect a small component in the detrital zircon population because provenances will not be uniformly distributed through time (Link et al. 2005; Sláma and Košler 2012; Košler et al. 2013).

Alternatively, given the inherent natural and artificial biases making true representation unlikely regardless of the number of single-grain analyses, a third approach is to combine both the quantitative (e.g., 35–70 grains) and qualitative strategies (Andersen 2005). A consensus on best practice in selecting the number of detrital zircon grains to analyze is yet to be resolved.

The two inherent features of U-Pb isotopic data are discordance and age-dependent precision which need to be accounted for in processing detrital zircon age data. It is typical, but subjective, to filter discordant data at 5 % or 10 % and step between calculating ages based on the $^{206}\text{Pb}/^{238}\text{U}$ ratio below 1,000 Ma and the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio above. Nemchin and Cawood (2005) suggest a more objective and reproducible method using the concordia age calculation (Ludwig 1998) on each individual analysis to combine $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages and provide a probability of discordance for weighting the precision.

Visualization

The growth of detrital zircon datasets presents challenges to visualize, interpret, and compare large quantities of age data.

Because standard Wetherill and Tera-Wasserburg concordia charts quickly become obscured with large amounts of scattered detrital zircon data, the typical approach is to use a single age variable – to visualize the data using histograms or density distributions (although there are alternative visualization tools, see Sircombe 2006).

The typical approach to visualizing detrital zircon data is the probability density distribution or plot created by summing a series of normal distributions with means and standard deviations based on individual analyzed ages and their uncertainties (originally applied to detrital zircon fission-track data by Hurford et al. (1984) and U-Pb age data by Dodson et al. (1988), but likely based on earlier work in Ar/Ar analysis, e.g., Jessberger et al. (1980)). Building on the observations of Galbraith

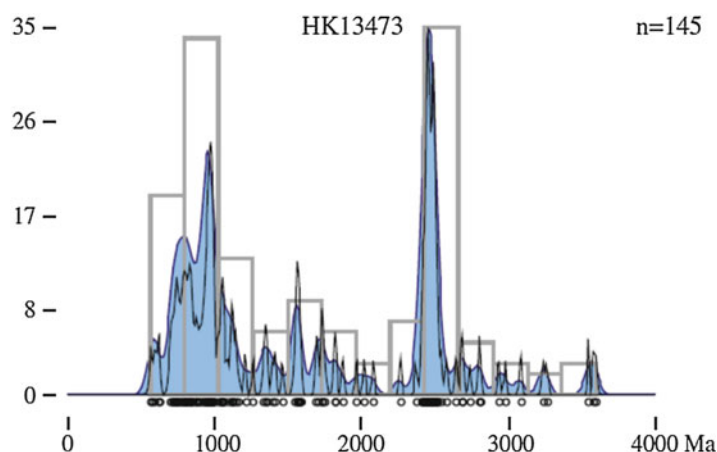


Fig. 2 Comparison of visualization tools for a set of detrital zircon U-Pb ages from Hong Kong. Kernel density estimations (KDE) in *blue-shaded areas*, probability density plots (PDP) in *black lines*, histograms in *light-gray rectangles*, and individual ages illustrated by *circles* along x-axis (From Fig. 4 of Vermeesch (2012))

(1998) with fission-track geochronology, Vermeesch (2012) explained that probability density distributions are not true density estimates and established a kernel density estimation visualization that sums a calculated and uniform distribution for each analyzed age (Fig. 2).

Interpretation

A common aim of detrital zircon analysis is to extract ages to correlate with potential protosources using objective and reproducible deconvolution methods such as the maximum-likelihood mixture modeling of Sambridge and Compston (1994) or Bayesian mixture modeling (Jasra et al. 2006).

Increasing volumes of detrital zircon geochronology data are driving greater use of comparison methods and measurements of similarity to investigate the relationships among samples. Simple “eye-ball” comparison of plotted detrital zircon age distributions is neither objective nor reproducible.

A commonly used similarity comparison method uses a Kolmogorov-Smirnov (K-S) goodness-of-fit test based on the maximum distance between the cumulative probability distributions of samples being compared (Berry et al. 2001). While broadly used (e.g., DeGraaf-Surpless et al. 2003; Amidon et al. 2005; Dickinson and Gehrels 2009), the K-S method is sensitive to proportions of components and may produce counterintuitive results (Gehrels 2012). Vermeesch (2013) also discusses that the *p*-value generated by a K-S test to test if a hypothesis is statistically likely or not may be too simplistic and vulnerable to sample size effects.

Increasingly complex methods have also been developed, such as kernel estimation functions applied to detrital zircon age distributions to calculate similarity and the probability of being sourced from the same population (Sircombe and Hazelton 2004). Principal component analysis has also been applied to large datasets (Sircombe 2000b), although Vermeesch (2013) discusses the mathematical constraints of this approach and develops a broader multidimensional scaling (MDS) method. This approach can illustrate potential relationships between samples and protosources with a visualization similar to geochemical mixing models (e.g., Fig. 3; Che and Li 2013).

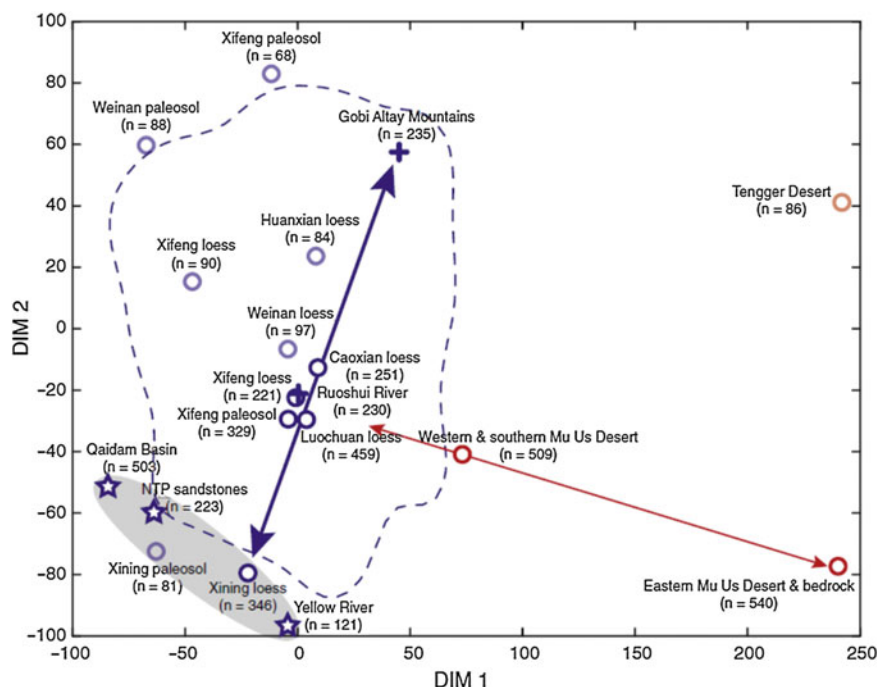


Fig. 3 Multidimensional scaling (MDS) map using the statistical technique of Vermeesch (2013) illustrating the similarity relationships between detrital zircon geochronology distributions in Chinese Loess Plateau samples (*blue circles*) and potential protosources (*blue stars* and *red circles*). *Blue arrow* shows possible binary mixing between sources in the Northern Tibet Plateau (NTP) and Gobi Altay Mountains (GAM) which are dominated by ~450 Ma and 350–250 Ma age modes, respectively. The *red line* shows the marked difference with samples from the Mu Us Desert (Stevens et al. 2013) which have dominant 200–100 Ma age modes (From Fig. 3 of Che and Li (2013))

Applications

Detrital zircon geochronology is applied to a wide range of geoscience questions (Fedó et al. 2003; Gehrels 2012), which can be broadly characterized as follows.

Geological Reconnaissance

Detrital zircons can provide useful geological insights into very broad regions such as desert sands in Central Australia (Pell et al. 1997) or ice-rafted drop stones in the North Atlantic Ocean (Small et al. 2013). Reconnaissance studies can also extend geological insight into regions that are physically obscured by ice in Antarctica (e.g., Goodge et al. 2002; Veevers et al. 2008; Palmer et al. 2012) or politically inaccessible (e.g., North Korea, Wu et al. 2007).

Stratigraphy, Chronostratigraphy, and Basin Evolution

A sequence of sedimentary units can provide critical information about the geological evolution of a sedimentary basin provided that the sequence can be adequately delineated through time. Detrital zircon geochronology can be used to provide an absolute chronological framework with maximum deposition ages and potential identification of disconformities, particularly in Precambrian rocks where biostratigraphy is limited.

The concept of a maximum age of deposition is based on the principal of inclusions – the deposition of the sediment itself must have occurred *after* the age of the youngest detritus in the

sediment. A cross-cutting relationship such as a dateable igneous intrusion can establish a minimum age of deposition (i.e., sediment deposition must have occurred *before* the intrusion).

However, the premise of the maximum age of deposition is founded on several assumptions, and seeking other lines of evidence to validate age bracketing of a sedimentary unit is advisable. The calculation of the maximum age itself from a given set of detrital zircon U-Pb age data can be conducted in several ways, yielding a wide variety of results (Dickinson and Gehrels 2009; Tucker et al. 2013).

There is no constraint on lag time between the formation of the youngest zircon and its deposition. Modern beach sand on the eastern Australia passive margin found a 250-million-year gap between the youngest zircon and modern deposition (Sircombe 1999). The assumed rapid transport of relatively young detritus into basins in active tectonic settings (Cawood et al. 2012) has been demonstrated for Mesozoic sequences from the Colorado Plateau that also have biostratigraphic constraints (Dickinson and Gehrels 2009). However, Cawood and Nemchin (2000) illustrate that tectonic activity can uplift and erode older sources just as readily as contemporaneous sources with a sequence of detrital zircon geochronology in the Perth Basin, Western Australia, where the stratigraphically youngest units have older apparent maximum deposition ages than stratigraphically older units.

Sudden change in detrital zircon age distributions can also be suggestive of hidden gaps in the sequence. This is demonstrated in the detrital zircon age distribution from a sequence of samples in the Paleoproterozoic Hurwitz Group in the western Hudson Bay region of Northern Canada that changes from Archean-dominated to a Paleoproterozoic-dominated with suggestions of a depositional hiatus of up to 150 million years (Fig. 4, Davis et al. 2005).

Provenance Analysis and Sedimentary Processes

Attempting to understand the provenance of sedimentary detritus also prompts greater understanding of the sedimentary processes transporting material between source and deposition. One recurring feature of detrital zircon geochronology is evidence of exceptional long and persistent transport pathways through geological history.

Building on lithostratigraphic indications of large river systems in Proterozoic Laurentia (Young 1978), analysis of detrital zircon in the Shaler Group on Victoria Island in the western Canadian Arctic revealed a prominent Mesoproterozoic component that is interpreted as being sourced from the Grenvillian Orogeny ~3,000 km away on the modern eastern margin of North America (Rainbird et al. 1992). Further work in similarly aged sedimentary units across North America has confirmed this premise and developed a model of a massive mountain building coupled with high rates/volumes of erosion and dispersion in an ancient environment with strong chemical weathering and lacking soil-binding vegetation (Rainbird et al. 2012; Fig. 5)

Another massive orogenic belt accompanied by rapid erosion and vast dispersion is seen in the widespread and often dominant occurrence of Neoproterozoic-aged zircon in Neoproterozoic to modern sedimentary basins throughout the former Gondwana supercontinent in Australia, India and the Himalaya, Africa, and South America (e.g., Ireland et al. 1998; Sircombe 1999; Avigad et al. 2005; Squire et al. 2006; Veevers et al. 2005a, b Myrow et al. 2010).

These extraordinary pathways are associated with environments prior to the evolution of terrestrial vegetation, but a modern analogue of a continental-scale sedimentary pathway is seen with the persistence of Cenozoic-aged zircon from the Andean orogenic margin thousands of kilometers downstream in the modern Amazon River (Mapes 2009; Lawrence et al. 2011).

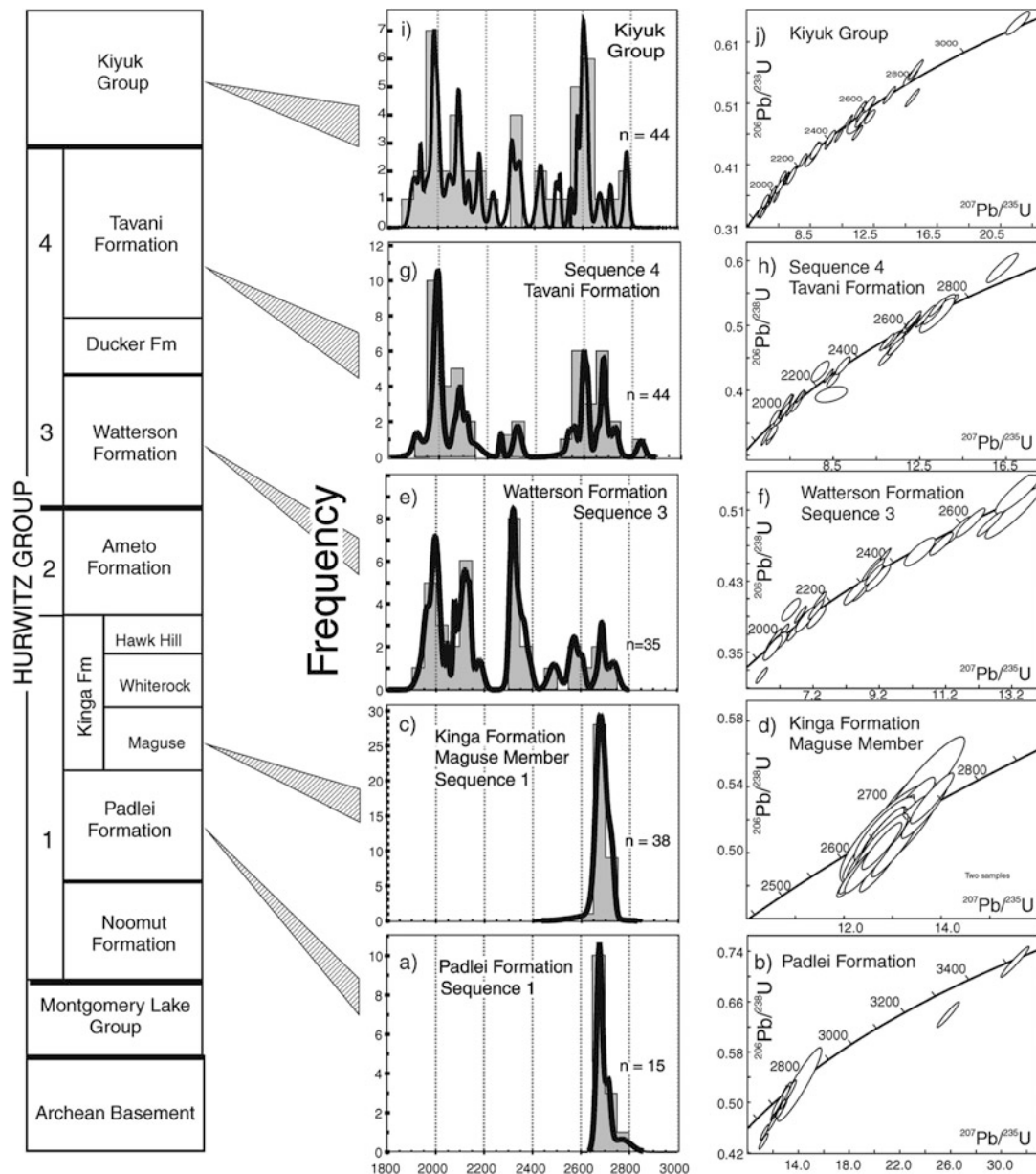


Fig. 4 Stratigraphic column of the Hurwitz and Kiyuk groups in the western Churchill Province, Nunavut, Canada, illustrating a marked change in detrital U-Pb zircon ages between the Kinga Formation and the Watterson Formation interpreted as a major change in sedimentary provenance (From Fig. 2 of Davis et al. (2005))

Tectonic and Paleogeographic Reconstructions

Detrital zircon age data have been applied in the last 20 years to testing and refining often controversial models of reconstructing the Rodinia supercontinent based on lithostratigraphic and paleomagnetic evidence (Li et al. 2008).

Examples of intercontinental correlation include:

- 1,610–1,500 Ma detrital zircon ages in the Mesoproterozoic Belt-Purcell Supergroup of western North America do not have a likely local source in contemporaneous Laurentia and are correlated

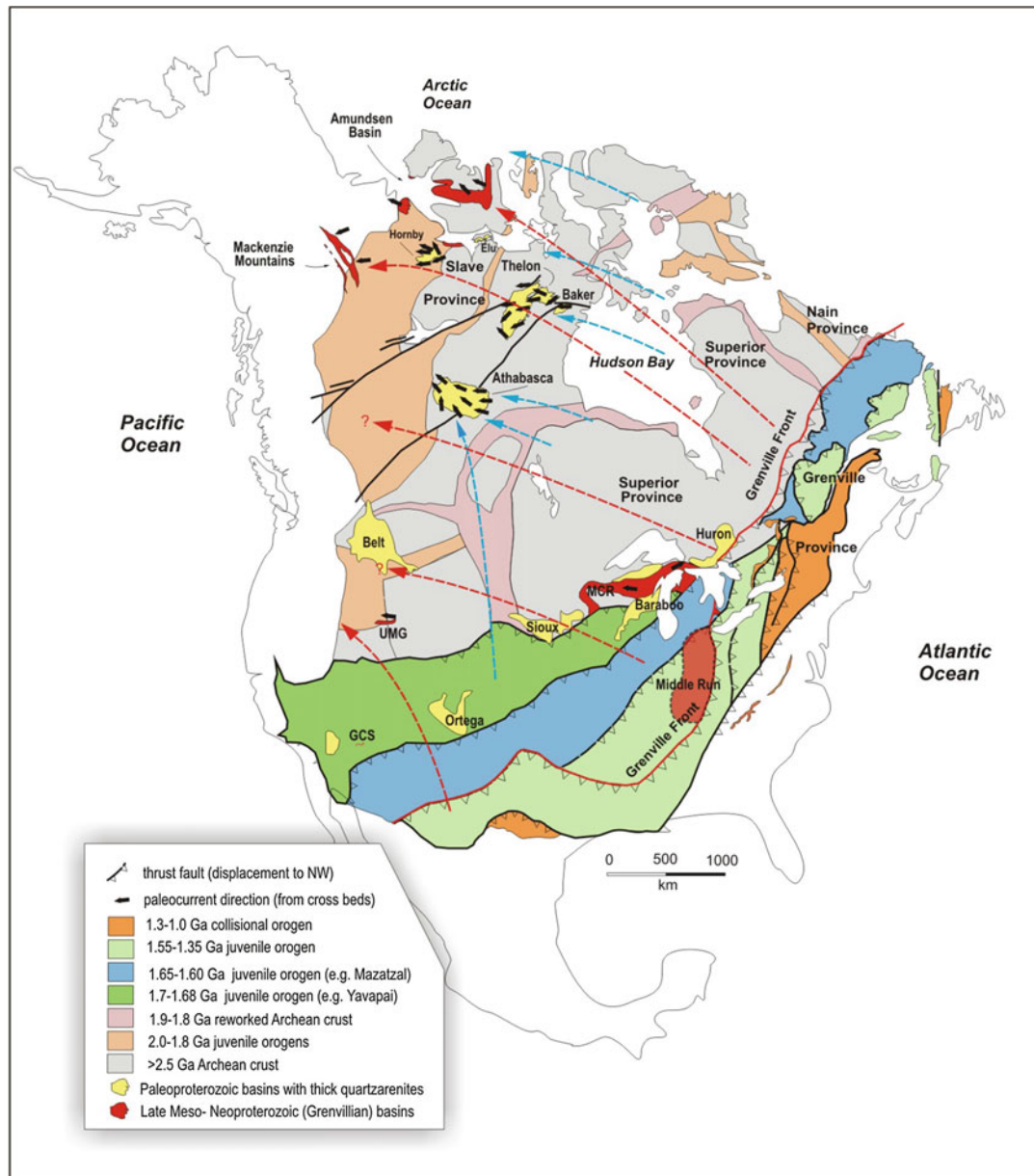


Fig. 5 Geological map of North America illustrating interpreted extremely long sedimentary pathways from Proterozoic orogens in modern southeast to basins in modern northwest based on detrital zircon geochronology (From Fig. 29.2 of Rainbird et al. (2012))

with protosource rocks of similar age in central and northeastern Australia (Ross et al. 1992; Blewett et al. 1998; Ross and Villeneuve 2003).

- Alternatively, 1,600–1,300 Ma detrital zircon in the Transantarctic Mountains of East Antarctica, along with other isotopic evidence, is linked with distinctive sources in Laurentia/North America to support the SWEAT (Southwestern United States and East Antarctica) model of Rodinia configuration (Goodge et al. 2004 and 2008). A more recent study of detrital zircons in the Belt-Purcell Supergroup suggests further modifications to this model (Stewart et al. 2010).
- The location of the South China block in Rodinia configurations is also controversial with some models placing it as the “missing link” between eastern Australia and Laurentia (Li et al. 2008).

Paleomagnetism supports this configuration, but because paleolongitude is unconstrained, alternative models with the South China Block linked with Northeastern India and Western Australia have been proposed (e.g., Yang et al. 2004). Detrital zircon analysis has provided further support for the latter models with noted age components in Neoproterozoic sedimentary units exotic to South China similar to those found in India and East Antarctica (Yu et al. 2008). The regional correlations may also persist into Gondwana reconstructions with detrital zircon in Paleozoic sedimentary units also sharing similarity with detrital zircon from units in Western Australia (Duan et al. 2011; Cawood et al. 2013b). Similarly, detrital zircon correlations are made between the Lhasa terrane in Tibet and northwestern Australia, suggesting a complex formation and breakup of the Gondwana margin through the Proterozoic and Paleozoic (Zhu et al. 2011).

Crustal Evolution

The ever increasing volume of detrital zircon age data can be used to explore broader questions about the evolution of the Earth's crust as a whole (Cawood et al. 2013a). The abundance of certain age components, albeit with an acknowledgment of possible sampling bias, is considered as a proxy for the volume of orogenic zircon-producing activity. Studies such as Condie et al. (2009a) and Voice et al. (2011) have collated up to nearly 200,000 individual detrital zircon analyses from around the world (Fig. 6). Prominent age components identified in these data indicate that crustal evolution is punctuated by episodic orogenic/magmatic events correlated with supercontinent amalgamation (Condie and Aster 2010). Apparent gaps in the distribution, such as around 2,450–2,200 Ma, may also be indicative of broader whole-earth processes (Condie et al. 2009b).

Early Earth

The discovery of Hadean-aged detrital zircon in the Narryer Terrane in Western Australia (Froude et al. 1983; Compston and Pidgeon 1986; Dunn et al. 2005) is a major achievement of detrital zircon geochronology. These rare grains provide a unique window into the geochemical processes of the earliest Earth, and considerable effort has been made to find and analyze more of these grains (Harrison 2009). The oldest terrestrial material analyzed to date is a detrital grain from the Jack Hills at $4,404 \pm 8$ Ma (Wilde et al. 2001). Hf and oxygen isotopic analyses of these detrital grains have been interpreted as indicating that continental crust had formed (Harrison et al. 2005) and a liquid hydrosphere was present at or near the surface (Mojzsis et al. 2001) within a few hundred million years of the Earth forming. Although evidence remains limited (Nutman 2001; Valley et al. 2006), these results are tantalizing because such surface conditions are considered prerequisites for the emergence of life. Further work is required, especially in other localities where occurrences of Eoarchean- and Hadean-aged detrital zircon have also been found such as:

- Beartooth Mountains, Montana (Mueller et al. 1998).
- Yilgarn Craton, Western Australia (Nelson et al. 2000; Crowley et al. 2005; Thern and Nelson 2011).
- Slave Craton, Northern Canada (Iizuka et al. 2006).
- Sao Francisco Craton, Brazil (Hartman et al. 2006).
- Several locations in China (e.g., He et al. 2011, Huang et al. 2013, and references therein).

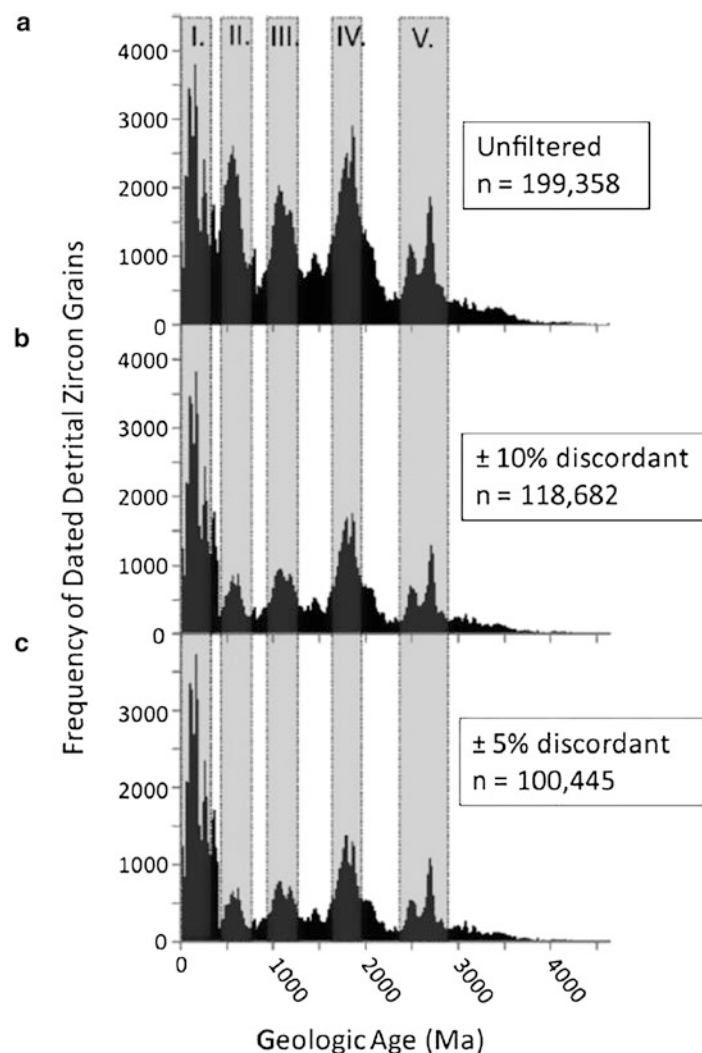


Fig. 6 A compilation of global detrital zircon age data illustrating the cyclical occurrence of prominent peaks at I. 300–100 Ma, II. 700–500 Ma, III. 1,200–1,000 Ma, IV. 2,000–1,700 Ma, and V. 2,700–2,500 Ma (From Fig. 1 of Voice et al. (2011))

Summary and Future Developments

The development of highly productive U-Pb analytical methods in the last 30 years has provided the tools for a wide range of researches into sedimentary provenance and basin evolution using detrital zircon geochronology. Applications include geological reconnaissance in large, poorly constrained regions and stratigraphic correlations building toward paleogeographic reconstructions of ancient supercontinents. Large-scale geochronology data acquisition also potentially provides information about global crustal evolution and has enabled the discovery of rare, but significant, remnant zircon from the Hadean Eon.

Detrital zircon geochronology provides insight into, and is in turn constrained by, an understanding of sedimentary processes and the potential for biasing. Although a common constituent of sedimentary rocks, zircon's typical petrogenesis in felsic igneous or metamorphic rocks limits the representation of mafic igneous events in a detrital age distribution. Processes of sediment formation

and transport have also been shown to bias distribution. Sample acquisition and processing needs to be carefully considered and monitored to avoid potential artificial biasing.

Although increasing acquisition of data brings new opportunities to compare and contrast a wide range of datasets, the volume of data being managed, visualized, and interpreted poses new challenges. Data visualization and interpretation tools have recently emerged, although further development is required to build toward standard usage of these tools.

Acknowledgments

Thanks to Natalie Kositcin, Chris Lewis, and Richard Blewett for the detailed and constructive reviews. This paper is published with the permission of the CEO, Geoscience Australia (GeoCat #76751).

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Age of the Earth

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Synonyms

Accretion time of Earth; Earth formation age; Planetary differentiation; Timing of core formation

Definition

Current constraints on the *age of the Earth* suggest accretion began approximately 4.54 ± 0.05 b.y. a., shortly after the formation of the solar system (~ 4.567 b.y.a.). However, the exact accretion time of Earth is difficult to determine, with predictions from different accretion models ranging from a few million up to about 100 m.y. after the formation of the solar system. Not surprisingly, our understanding of the *age of the Earth* is deeply rooted in our overall understanding of planetary science, particularly in our ability to accurately date meteorites using various radiogenic chronometers (e.g., U–Pb). The present-day best estimate for the *age of the Earth* is not decidedly different than the initial estimate of 4.55 ± 0.07 b.y.a. made by Patterson in his pioneering 1956 work. However, the resolution of the U–Pb isotope system is still not high enough to distinguish between very small age variations that may potentially separate the Earth, planets, and planetary bodies (e.g., meteorites). As a result, the exact timing of Earth formation is still a hotly debated issue, due in large part to the fact that the first ~ 500 m.y. of Earth history are not well preserved (Halliday 2004) in the terrestrial rock record. The oldest known materials on Earth are zircons from Western Australia, dated at 4.404 ± 0.008 m.y. (Wilde et al. 2001); however, terrestrial data of this age are limited and as a result this time period is shrouded in mystery.

In order to circumvent the lack of data available for early Earth history, geochronologists rely heavily on theoretical modeling and limited geochemical constraints from short-lived radionuclides to decipher the absolute timing of Earth formation. Xenon (^{129}Xe and ^{136}Xe) excesses in Earth's atmosphere suggest identifiable contributions from the decay of the short-lived radionuclides ^{129}I and ^{244}Pu , but in quantities considerably lower than predicted from abundances observed in meteorites. This implies that Earth did not achieve isotopic closure of the I–Pu–Xe system until ~ 100 m.y. after the formation of the solar system (Pepin and Porcelli 2006), an observation in agreement with $^{235}\text{U}/^{238}\text{U}$ – $^{207}\text{Pb}/^{206}\text{Pb}$ chronological methods (Allegre et al. 1995).

A slightly different approach is to use the onset of differentiation and core formation to define the exact *age of the Earth*. In this regard, the U–Pb and ^{182}Hf – ^{182}W isotope systems are the most useful as they can potentially reveal information about the timing of core formation. However, these chronometers are unable to differentiate between early accretion coupled with late core formation and late accretion coupled with simultaneous core formation. Nonetheless, the ^{182}Hf – ^{182}W system unambiguously dates core formation between 10 and 15 m.y. after the

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formation of the solar system (Halliday 2004; Yin et al. 2002) and, as a result, indirectly constrains accretion timescales.

Accurately dating the Earth's age is a fundamental objective of Earth science and only with continued work will the opposing models be fully reconciled with one another. However, at present, the best age of Earth remains ~4.54 b.y.

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Luminescence Dating, History

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Definition

Luminescence dating is based on the perception in solid state physics that energy from the absorption of ionizing radiation can be stored in the crystal lattice of insulators as radiation damage. Thermal or optical stimulation of dosed mineral grains results in release of radiation-induced luminescence. The amount of radiation damage and, thus, the acquired luminescence signal is at least within certain limits, proportional to the time during which the insulating minerals were exposed to ionizing radiation. Assuming a constant rate of natural ionizing radiation the age is calculated as the ratio of the accumulated dose over the dose-rate. The present contribution deals with the history of luminescence dating from the first observations of the luminescence phenomenon via the first proposal to use it for dating purposes, and the first dating application to the present wide field of applications in archaeology, Quaternary geology, geomorphology and geoarchaeology.

Early observations of the phenomenon

The term “Luminescenz” was first used in 1888 by the German physicist Eilhardt Wiedemann at the University of Erlangen for “all those phenomena of light which are not solely conditioned by the rise in temperature,” i.e., the condition of incandescence or “hot light” in contrast to luminescence or “cold light” (cited after Harvey 1957). He differentiated various kinds of luminescence according to the method of excitation or of stimulation, such as photoluminescence, thermoluminescence, triboluminescence and chemiluminescence. When irradiating various minerals with “Entladungsstrahlung” (cathode rays) Wiedemann and his colleague Gerhart Schmidt (Wiedemann and Schmidt 1895) observed, after gentle heating, a light-emission and thus first described the phenomenon of “thermoluminescence” (TL), which is a thermally stimulated radioluminescence induced by ionizing radiation. Experiments with the phenomenon of luminescence led in the same year to the epochal discoveries of X-rays by Conrad Roentgen at Würzburg and of the natural radioactivity by Henri Becquerel at Paris only 1 year later.

Actually, a luminescence phenomenon had been already scientifically described more than 200 years before by Robert Boyle. He reported on 28 October 1663 to the Royal Society “About a diamond that Shines in the Dark” and adding experimental details, particularly “I also brought it to some kind of Glimmering Light, by taking into bed with me, and holding it to a good while upon a warm part of my Naked Body” (cited after Aitken 1985). A few years later Johann Sigismund Elsholtz (1676) at Berlin described a similar property for the mineral fluorspar. There are also much

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earlier reports on luminescent gems and stones which glimmer in the dark after being exposed to light, probably a kind of photoluminescence (Harvey 1957).

Evolution of TL dating: from first suggestions to first results

It was Farrington Daniels and coworkers at the University of Wisconsin in 1953, while measuring exposure of minerals to nuclear radiation, who first proposed to use thermoluminescence also for geological and archaeological age determination (Daniels et al. 1953). Ceramics and burned bricks, mainly from the Roman period, were the first archaeological materials on which the suggested method was successfully tested by Norbert Grögler and colleagues at the University of Bern (Grögler et al. 1958, 1960), followed by Kennedy and Knopff (1960) at the University of California. Starting from this point, luminescence dating gradually evolved into a powerful tool for heated archaeological materials. This was mainly due to the efforts by Martin Aitken and his team at the University of Oxford during the 1960s (Aitken et al. 1964, 1968b, cited after Aitken 1985), but gradually also other laboratories became involved. The essential procedures of pottery TL-dating were developed: the quartz inclusion technique (Fleming 1966) and the fine-grain technique (Zimmerman 1967). An important by-product of these methodological developments was the TL authenticity-testing of ceramic objects (Fleming et al. 1970). In addition to baked clay, TL dating has been also applied to heated stones, in particular to flint artefacts (Göksu et al. 1974).

Dating of Sediments

With the recognition that not only heating, but also optical bleaching resets the TL signal (Wintle and Huntley 1979), the method became also applicable to the dating of sediments. The observation made on quartz that intense green illumination, instead of heating, also stimulates luminescence (Huntley et al. 1985) opened the door for utilizing the phenomenon of Optically Stimulated Luminescence (OSL) for dating. Soon afterwards the luminescence stimulation by infrared illumination of feldspar was discovered (Hütt et al. 1988).

TL Dating of Sediments

The observation that the natural TL intensities from Quaternary sediments increase with geological age stimulated researchers from the former USSR to propose TL as a tool for the chronology of sediments. Pioneer research was done by V. N. Shelkopyas and G. V. Morozov at Kyiv (Dreimanis et al. 1978). The lack of English publications by the Kyiv group makes it difficult to fully understand sample preparation and measurement protocols. The apparently most important early work is noted in Morozow (1968) and Shelkopyas and Morozow (1981) even if a first note by Shelkopyas and Morozow (1965) dates a few years earlier. Favourable material for the Kyiv group was loess from which they first tried to establish a relative TL chronology by a kind of regeneration of the natural signal using X-rays or γ -irradiation. Later, numerical ages were calculated assuming that almost all relevant natural growth of the TL signal was due to natural alpha irradiation but this idea was revised by Shelkopyas and Morozow (1981) accounting for an alpha efficiency of ca. 0.1. A fully reliable TL dosimetry satisfying modern requirements (e.g., Aitken 1985; Guerin et al.

2011) was not delivered in the early work at Kyiv. But also the estimation of the equivalent dose ED remained questionable. Thus, Wintle and Huntley (1982) doubted the reliability of these TL ages.

Despite this, several merits of the early work at Kyiv and some technical details deserve mention. The heating rate was only 1 K/s up to 300 °C or 350 °C. Photomultipliers of the Russian type FEU-19 and FEU-29 with maximum sensitivity at ca. 380 nm were used for detection. The peak of the natural TL was found at ca. 230 °C hotplate temperature. Despite the lack of rigorous physical and chemical mineral separation the Kyiv group dubiously stated that the TL signal was obtained from quartz grains. Experiments using coarse (1 mm) as well as small ground “quartz” grains (0.01 mm) showed much smaller TL from fine grains. Although resetting of the TL signal by UV light was also observed, Morozow (1968) concluded that triboluminescence due to weathering and transport was the main factor to reset the inherited TL signal. Wintle and Huntley (1979, 1980) first demonstrated that sunlight exposure bleaches the TL signal of sediments which, however, does not rule out the effect of triboluminescence.

Clearly, the merits of the early work done in Kyiv are to have shown the capability of TL from sediments to establish a relative and stratigraphically consistent chronology from Quaternary sediments. For details of further development of TL sediment dating we refer to Wintle and Huntley (1982).

The work by Wintle and Huntley (1979, 1980) boosted the development of TL dating for sediments. Since daylight bleaching was identified as the main resetting mechanism further work concentrated on TL dating of wind-lain sediments, in particular loess and dune sands. But also fluvial and coastal sediments were tested. Special attention was directed to determine the unbleached residual of the TL at deposition to circumvent age overestimates. The originally applied “R-Γ” respectively “R-β”-method (Wintle and Huntley 1980) was complemented by additive and regenerative “total bleach” methods for aeolian sediments of middle and lower latitudes for which a resetting of the TL at deposition to an unbleachable residual was assumed. Further “partial bleach” methods to account for partial resetting at deposition were proposed by Mejdahl (1985). Meanwhile refined techniques for TL dosimetry allowing for calculation of more accurate and reliable effective dose-rates (e.g., Aitken 1985; Mejdahl 1979) contributed further steps towards meaningful TL ages of sediments. The “feldspar inclusion technique” (Mejdahl 1983) was extended to dating of sediments and, thus, advantage was taken from dating of different mineral phases with different TL characteristics.

The euphoria at the early 1980s was dampened beginning in 1985 when significant TL age underestimates from loess older than 30–100 ka (1,000 years ago) became obvious from many publications. The poorly understood phenomenon of “anomalous fading” from feldspars was often made responsible for this, but some authors claimed that reliable ages up to 300 ka or even 800 ka could be obtained (e.g., Singhvi et al. 1989; Berger et al. 1992). To some extent, non-standardized laboratory protocols contributed to the uncertainty. Zöller et al. (1988, 1991) demonstrated that the reliable TL age range from loess could be extended to a minimum of about 100 ka. Besides the “effective mean lifetime” τ of an electron trap (c.f. Wagner 1998), “dose-dependent sensitivity change” (Wintle 1985) was suggested to explain observed age underestimates from older loess. Finally, efforts were made to additionally investigate the characteristics and stability of luminescence centres using a CCD camera-based luminescence spectrometer (Rieser et al. 1994).

On the other hand, the risk of TL age overestimates from sediments due to incomplete optical resetting (often referred to as incomplete bleaching) at deposition gave increasing distinction to the discussion. This resulted in the development of OSL dating (Huntley et al. 1985; Hütt et al. 1988; Aitken 1998). Finally, the TL dating of sediments was almost completely abandoned since the mid-

1990s. Some laboratories, however, have continued with TL dating of loess and have published reasonable results even for loess >200 ka (Kuziak et al. 2007).

Recent developments of TL dating

TL dating of burned flint as direct dating of ancient human activity has been an important application since 1974 (Göksu et al. 1974). Recent developments, including microdosimetry problems of some flint tools, are described in Richter (this volume). Successful TL dating results for volcanic eruptions using quartz, feldspars or volcanic glass are reviewed by Fattahi and Stokes (2003). The more recent availability of band-pass filter glasses for detecting luminescence emissions in a narrow wave-length band has resulted in the intensified use of orange-red emissions (ca. 620 nm) from quartz. Despite the disadvantage of a much lower signal/noise ration the great advantage of the 620 nm emission from quartz is its high saturation dose which exceeds the saturation dose of UV-A (315–400 nm wavelength) or blue emissions by more than an order of magnitude. Meaningful TL ages >1 Ma using the orange-red emission from quartz appear obtainable (Fattahi and Stokes 2000). As volcanic quartz is not a significant component in most mafic rocks, Zöller and Blanchard (2009) used heated crustal xenoliths and maar tephra for TL dating, but different techniques yielded diverging ages so far, which points to pending problems. TL dating of baked loess from a Lower Gravettian hearth in Austria, however, resulted in congruent ages obtained from blue TL emission of polymineral fine grains and orange-red emissions from quartz separates in agreement with results from independent dating methods (Zöller et al. 2013). Aeolian quartz grains baked by lava flows were successfully dated to ca. 170 ka using orange-red TL emissions (Suchodoletz et al. 2012).

Surface Dating

In addition to sediment dating, it is also possible to determine the age when the surface of a stony object, which had been exposed to daylight before, became ultimately shielded from light. This allows dating various archaeological and geological events, such as the construction as well as the destruction of stone buildings, the burial of stone artefacts and the sedimentary deposition of boulders. Liritzis (1994) proposed to use TL to date the construction of a megalithic limestone building. But the applied methodology was hampered by the fact that in calcite – even after extended exposure to sunlight – retains a significant residual TL signal (Liritzis and Galloway 1999). As in sediment dating, this problem of unbleachable luminescence signals is overcome by the use of OSL instead of TL. It seems, therefore, consequent to employ OSL dating also to stone surfaces. Early attempts to determine the burial age of quartzite pebbles by this approach were reported by Huntley and Richards (1997). After scraping off the uppermost part from the bleached surface of lithic artefacts, IRSL dating was applied to the fine-grained feldspar fraction, whereby uncertainties with insufficiently bleached grains were encountered (Morgenstein et al. 2003). When utilizing a high spatial resolution OSL-detection technique (HR-OSL) of minerals that are left in their original petrologic context, i.e., without any mineral separation, Greilich et al. successfully dated a stonewall of the medieval castle of Lindenfels, Germany, and the pre-Columbian Nasca lines (geoglyphs) around Palpa in southern Peru (Greilich et al. 2002, 2005).

Perspectives of TL Dating

The appropriate method for age determination of sediments is presently optical dating, in particular for young sediments. The upper age limit of optical dating is, despite more recent attempts using post-IR-IRSL (pIR-IRSL) or Thermal Transfer-OSL (TT-OSL) dating, hampered by either low saturation doses or by age underestimates. As for older sediments the unbleached TL residual becomes increasingly negligible, TL dating protocols deserve further attention. The more promising application of TL dating will, however, be concentrated on heated materials such as artefacts or rocks heated by, e.g., volcanic eruptions.

Recent developments of OSL and IRSL dating

As IRSL and, in particular, OSL minimizes the problem of age overestimates due to unbleached residuals at deposition, the rapid development of OSL dating enabled the assessment of reliable chronologies of sediments from Late Glacial and Holocene and of archaeosediments. The Single Aliquot-Regeneration (SAR) protocol (Murray and Wintle 2000) became soon established as a routine protocol. High resolution deciphering of landscape development under the influence of mankind not only supplied chronostratigraphies of geoarchaeological sites but also initiated further development and verification of geomorphologic and geoarchaeologic concepts (e.g., Lang and Hönscheid 1999; Lang et al. 1999; Fuchs et al. 2004).

The very rapid bleaching of quartz-OSL and the application of statistical methods to discriminate between well and poorly bleached sub-samples measured by the SAR protocol opened up the ability to obtain meaningful dating results from sediments or geomorphologic events not datable by luminescence before, such as periglacial slope deposits (Hülle et al. 2009) or tsunamites (Brill et al. 2012). The rather low saturation dose of quartz-OSL, however, limits the upper dating range to less than or around 100 ka, depending on the natural radioactivity of the sediment. The much higher saturation dose of feldspar-IRSL may allow for an upper dating limit of 200–300 ka or even more, but the limiting factor was found in the phenomenon of “anomalous fading,” an athermal long term instability of the luminescence from feldspars first described by Wintle (1973). Procedures to correct for anomalous fading were proposed by Huntley and Lamothé (2001) and Auclair et al. (2003) but they are expected to yield reliable results only in the linear part of the dose–response curve. More recently, the “post IR-IRSL” (pIR-IR) protocol was developed and tested (Buylaert et al. 2009, 2012; Thiel et al. 2011; Murray et al. 2013). It was found that the fading of the pIR-IR signal is significantly lower allowing reasonable age estimates of a few hundred ka. To extend the dating limit of quartz OSL by an order of magnitude a “Thermal Transfer-OSL” (TT-OSL) protocol using recuperated OSL was suggested (Wang et al. 2006, 2007; Porat et al. 2009) but results from testing the protocol still appear ambiguous (e.g., Zander and Hilgers 2013).

Perspectives of OSL and IRSL Dating

On the one hand, the new methodological developments of OSL dating as well as technical improvements of the luminescence readers enable dating of sediments deposited as young as a few years or decades. Thus, luminescence dating is ready for bridging the gap between historical geology (dating of past events) and process geomorphology (estimation of recent process rates). On

the other hand, the extension of the dating range beyond 100 ka towards 1 Ma remains a challenge, but first promising steps are breaking new ground.

OSL dating of rock surfaces (i.e., last exposure to daylight) is expected to gain increasing relevance for archaeology and geomorphology, in particular since the latest developments of commercial luminescence readers provide the option of spatially resolved luminescence measurements.

Infra-Red Radiofluorescence Dating

Although the infrared radiofluorescence (IR-RF) technique follows the same basic principles as TL and OSL dating, its dose determination differs from them. The underlying phenomenon is unequivocally a fluorescence effect (Krbetschek et al. 2000), and thus the original name was later changed from “radioluminescence” to “radiofluorescence” (Erfurt and Krbetschek 2003). IR refers to the near infrared emission (865 nm), which is characteristic for potassium feldspars, such as microcline and orthoclase. The physical background and radiation-dose dependence of this phenomenon have been intensively investigated, along with the methodological aspects of dating Quaternary sediments (Degering and Krbetschek 2007). Of particular interest for the data presented is the long-term stability of the IR-RF signal. It is possible to obtain IR-RF ages in agreement with independent age controls back to ~700 ka, such as demonstrated for the type-site of *Homo heidelbergensis* at Mauer, Germany (Wagner et al. 2010).

Further Reading

Further reading is recommended: Duller (2008), Preusser et al. (2008), Roberts (2008), and Wintle (2008). Periodicals informing about latest progress in luminescence dating are mainly *Ancient TL*, *Archaeometry*, *Quaternary Geochronology* and *Radiation Measurements*. Proceedings of the triennial international conference on Luminescence and ESR Dating (LED) are published in special volumes of *Quaternary Geochronology* and *Radiation Measurements*.

Summary

Within the last ca. 50 years the development of luminescence dating has been fast-paced. Originally, thermal stimulation (TL) was applied to date ceramics and heated artefacts. Later, the recognition of solar resetting of the luminescence signal broadened the application of luminescence dating strongly in a sustainable matter. For the first time, the sedimentation age of Quaternary sediments could be dated directly, first by TL and then later by optical stimulation (OSL). Beyond archaeology, luminescence dating has developed to become an indispensable scientific tool in Quaternary geology, geomorphology, and geoarchaeology world-wide. Challenges for ongoing research appear to focus on extension of the dating range towards the more recent as well towards older dating limits.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Chert](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating - General Principles](#)
- ▶ [Feldspar](#)
- ▶ [Geochronology](#)
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- ▶ [Quartz](#)
- ▶ [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)
- ▶ [Radiation Defect](#)

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Magnetic Chronology

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Definition

Study of the variations with time of the Earth's magnetic field by the analysis of direction and intensity of magnetization recorded by rocks, sediments, and archaeological materials and its use for dating and chronological correlation purposes.

Variations of the Earth's Magnetic Field

The present-day magnetic field at the surface of the Earth can be well approximated by an inclined magnetic dipole placed at the Earth's center which forms an angle of $\sim 11.5^\circ$ with the rotation axis. Such a dipole accounts for nearly 90 % of the field at the Earth's surface. The still significant amount remaining can be described by the non-dipole field. The Earth's magnetic field (EMF) is, however, not static, as its direction and strength vary with time. This field variability spans time scales ranging from fractions of a second to millions of years. The short-term variations arise mostly from currents flowing in the ionosphere and magnetosphere. The slower changes are produced by the so-called main field, which is generated by magnetohydrodynamic processes in the Earth's liquid iron outer core, and display periods of a year to millions of years. Periods of internal origin of an order shorter than a year cannot be detected at the Earth's surface because of the screening effect of the lowermost mantle (e.g., Merrill et al. 1998). Since a magnetic field has existed on the Earth since early in its history (e.g., Tarduno et al. 2010) and its direction and intensity vary with time with a broad spectrum of frequencies, it can be used as a dating tool on very different time ranges.

According to their magnitude, length, and global or regional character, different types of variations of the EMF can be distinguished. Variations of both direction and magnitude with periods ranging between years and tens of thousands of years are termed secular variation (SV). SV can be described as produced by the combined effect of variations in the dipole field and changes in the strength and location of the non-dipole field components. The former are synchronous on a global scale and are characterized by longer periods, while the latter vary over smaller distances and display shorter periods. As a result, patterns of SV are similar over subcontinental regions but differ markedly between continents.

Besides secular variation, one of the main characteristics of the EMF is that it switches its polarity, interchanging the positions of magnetic north and south. The duration of geomagnetic polarity intervals is rather variable, ranging between some tens of thousands and several millions of years. The term polarity chrons is used for the main subdivisions of time recognized on the basis of polarity, while short (0.1 Ma) polarity intervals occurring within a chron are termed subchrons (Harland et al. 1990). Periods of stable polarity are interrupted in several occasions by short-lived geomagnetic "events" of a few thousands of years of duration (e.g., Laj and Channell 2007) called excursions.

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Paleomagnetism

Detailed records of geomagnetic secular variation are only available for the last 400 years (Jackson et al. 2000), but there are no direct surviving observations of the EMF prior to this period of historical observations. Thus, information about characteristics and variations of the ancient geomagnetic field has to be obtained indirectly. Both rocks and archaeological materials can carry a remanent magnetization that is in most cases parallel to the field in which they were magnetized, so that its measurement can supply the direction of the EMF vector in the past. The determination of the ancient magnetic field by studying the magnetization recorded in rocks or other materials led to the development of paleomagnetism (e.g., Butler 1992; Tauxe 2010, which are good introductory books on this subject).

Rocks (or archaeological materials like ceramics or bricks) are assemblages in which fine-grained ferromagnetic minerals are dispersed within a matrix of diamagnetic and paramagnetic minerals. The stability of remanent magnetization is largely dependent on the grain size of these ferromagnetic minerals. Thermal oscillation leads to magnetic relaxation, in which remanent magnetization of an assemblage of grains decays with time. The most stable magnetization occurs in particles with single-domain (SD) state, characterized by a uniform magnetization. Less stable magnetization is carried by larger particles which are not uniformly magnetized and are referred to as multidomain (MD) grains. Very small uniformly magnetized ferromagnetic grains are, however, in a superparamagnetic state and are only able to produce a rapidly decaying short-lived remanent magnetization. On the other hand, remanent magnetization carried by SD grains can remain stable without decaying for time spans of the order of magnitude of the age of the Earth.

There are different mechanisms leading to the acquisition of a remanent magnetization. A thermoremanent magnetization (TRM) is acquired when a material is cooled down from above its Curie temperature in the presence of a magnetic field. The Curie temperature is a temperature characteristic of each ferromagnetic mineral type above which it loses its ability to preserve a remanent magnetization. A TRM is parallel to the ambient geomagnetic field direction during remanence acquisition and is typically found in igneous rocks or archaeological materials which have been subjected to firing (e.g., pottery, bricks, or kilns).

A detrital remanent magnetization (DRM) is acquired during deposition of sedimentary rocks. During deposition in a quiet environment, magnetized particles that can rotate freely will turn into the direction of the applied geomagnetic field like compass needles and will be subsequently locked in place during lithification. The formation of sedimentary rocks is, however, rather complex, and remanence acquisition may be affected by a variety of conditions and processes, like a diversity of initial mineralogies, perturbations during sediment deposition, Brownian motion of magnetized particles, flattening into the bedding plane by compaction, post-depositional modification through the action of organisms, or diagenesis. A remanent magnetization acquired due to physical alignment processes after deposition but before consolidation is usually termed post-depositional remanent magnetization (pDRM).

Relaxation time of small superparamagnetic grains can be dramatically increased by augmenting their grain size. Chemical changes that form ferromagnetic minerals which grow large enough in a magnetizing field create a chemical remanent magnetization (CRM) if this chemical changes take place at temperatures not as high as to produce a TRM. Chemical reactions giving rise to new ferromagnetic minerals include the alteration to a ferromagnetic mineral of a preexisting one and the precipitation of a ferromagnetic mineral from a solution. Very often CRM is a secondary magnetization, not acquired during rock formation but long after.

Paleointensity

Although in many paleomagnetic studies only directional information about the geomagnetic field is needed, its intensity also contains valuable information concerning field variability. Therefore, several investigations also demand the knowledge of the strength of the paleofield vector, which is called the paleointensity. Its determination is more difficult, since the magnitude of the paleofield vector cannot be directly read from the magnetization vector. While the direction of magnetization is, in most cases, parallel to the direction of the applied field, its magnitude is only proportional to the field intensity and only if the latter is low, like in the case of the geomagnetic field. In order to retrieve the strength of the magnetizing field, experiments which try to duplicate the acquisition of remanent magnetization in a known field have to be carried out. Complex remanence acquisition mechanisms like the ones creating CRM or DRM are, however, almost impossible to reproduce exactly in laboratory experiments. TRM acquisition, on the other hand, is easier to reproduce in laboratory experiments and well supported by a theoretical basis (Néel 1949; 1955). If a TRM_a was acquired by a rock in an ancient geomagnetic field B_a , TRM_a should be proportional to B_a . In the laboratory, a new TRM_{lab} can be imparted to the rock in a known field B_{lab} . If the proportionality constant between magnetizing field and magnetization is in both cases the same, the strength of the ancient geomagnetic field $B_a = B_{\text{lab}}(\text{TRM}_a/\text{TRM}_{\text{lab}})$. This experimental procedure is the foundation of the initial and most reliable technique for absolute paleointensity determination (Thellier and Thellier 1959). Fired archaeological materials and volcanic rocks should be therefore most suitable to determine absolute paleointensity.

DRM or pDRM acquisition is a complex process that cannot be reproduced exactly in laboratory experiments. Non-field effects like mineralogy and amount or magnetic domain state of the ferromagnetic materials present in a sedimentary sample must be removed from the magnetization signal in order to isolate the dependence of DRM on the ancient geomagnetic field intensity. Typically, the intensity of the remanent magnetization of a sample is divided by a factor that is sensitive to the amount of remanence-carrying grains present in the sample, like magnetic susceptibility or specific laboratory-induced remanence types. The normalized DRM or pDRM obtained this way will at best reflect the relative intensity of the applied geomagnetic field and is termed relative paleointensity. Results from globally distributed records allowed the construction of weighted averages of many relative paleointensity records which can be used as dating and millennial-scale correlation tools (e.g., Guyodo and Valet 1999), and ongoing studies are extending paleointensity stacks further back in time (e.g., Valet et al. 2005).

Magnetic Chronology

Time variations of the EMF take place in a wide range of periodicities, and the determination of polarities, directions, and intensities of remanent magnetization in paleomagnetic and paleointensity studies can be used as a powerful chronological tool. Magnetic chronology methods and techniques differ, however, according to the age and thus the time resolution needed.

Geomagnetic Polarity Reversals

One of the main characteristics of the Earth's magnetic field is that it has reversed its polarity many hundreds of times. A polarity reversal is a global event, experienced simultaneously all over the Earth. Thus, geomagnetic reversals provide a convenient means of stratigraphic correlation and dating. The correlation of polarity intervals with biostratigraphic stage boundaries associated to

radiometric ages yields a dated geomagnetic polarity time scale (GPTS) (Fig. 1). The development of the GPTS was initiated in the 1960s combining polarity data from globally distributed Pliocene-Pleistocene igneous rocks with ages obtained from the newly developed potassium-argon (K–Ar) dating method (e.g., Cox et al. 1964). The precision of the radiometric dating put, however, a practical limit to the application of this technique, as the error in determining the age of a lava sample that is about 5 Ma old was longer than the duration of many short events. The paleomagnetic study of deep-sea cores, in which sedimentary horizons could be paleontologically dated, allowed extending the polarity time scale into the Miocene (e.g., Opdyke et al. 1974). More recently, stratigraphic sequences have also been dated using climatically induced changes in lithology or stable isotopic records in sediments that are caused by variations in the Earth's orbit around the sun. This method is known as astrochronology, and astronomical tuning has allowed for a much more detailed and accurate chronology for the younger Cenozoic polarity reversals (Shackleton et al. 1990).

Seafloor spreading has created sequences of lineated marine magnetic anomalies in the ocean basins which provide the most complete and detailed record of geomagnetic polarity in the time interval between Middle Jurassic – the oldest seafloor – and present. Investigations of magnetic anomalies in all major oceanic areas yield a clear, consistent record of the history of geomagnetic polarity during the past 155–160 Ma. (e.g., Lowrie 2007a, b and references therein; Fig. 1). Because the age of the oldest seafloor is about 180 Ma and magnetic anomalies in these areas display subdued amplitudes, early polarity intervals have to be verified using magnetostratigraphic sections obtained from land exposures (e.g., Channell et al. 1995). Knowledge of geomagnetic polarity history older than late Jurassic is, however, still irregular.

The GPTS is a useful tool for dating stratigraphic sequences. By measuring the magnetization recorded in samples from a section and correlating the obtained polarity pattern to the GPTS, a precise temporal framework for the studied sequence can be obtained. This procedure is called

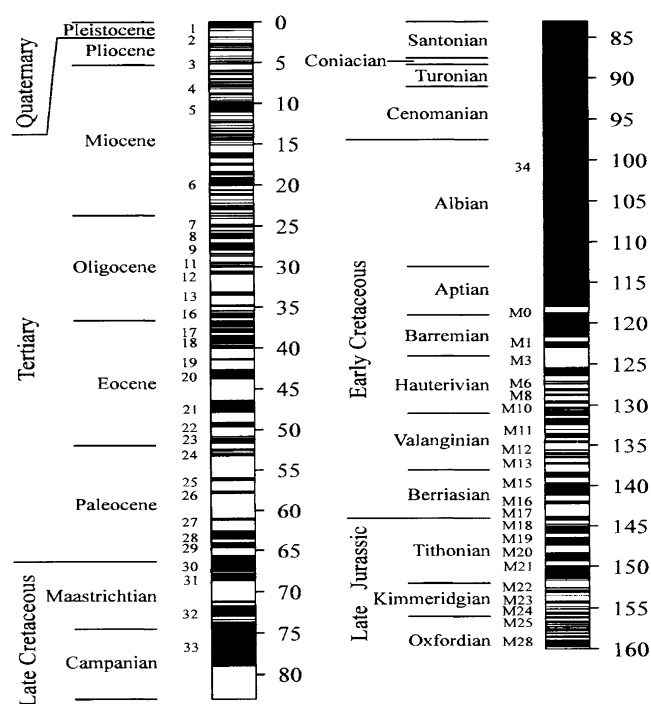


Fig. 1 Geomagnetic polarity time scale with magnetic anomaly numbers for the past 160 Myr (Figure from Merrill et al. 1998)

magnetostratigraphy (e.g., Opdyke and Channell 1996), and it allows correlating stratigraphic information on a global basis. Although the number of polarity reversals occurred during the Quaternary is small, their study has also been useful by providing a temporal reference in studies concerning hominin presence (e.g., Parés and Pérez-González 1995; Calvo-Rathert et al. 2008).

Geomagnetic Excursions

Recognition of brief polarity excursions as a part of the Earth's paleomagnetic field behavior has developed during the last two decades together with astrochronological calibration of the polarity time scale. During this time, numerous geomagnetic excursions have been discovered in the previously believed stable last two chrons, Brunhes and Matuyama (e.g., Laj and Channell 2007), although their number is still a matter of debate. Singer et al. (2002) propose the development of a geomagnetic instability time scale (GITS) for the Brunhes and late Matuyama chrons (Fig. 2).

Although theoretically geomagnetic excursions could be a useful correlation and dating tool in Quaternary stratigraphy, their utilization can be rather problematical. Questions like if they are local or global in extent or if they are mainly due to dipolar or non-dipolar field variations (e.g., Roberts 2008) can impose severe limitations to their applicability to chronological purposes. Merrill and McFadden (2005) recommend the use of excursions as a correlation tool only for locations separated

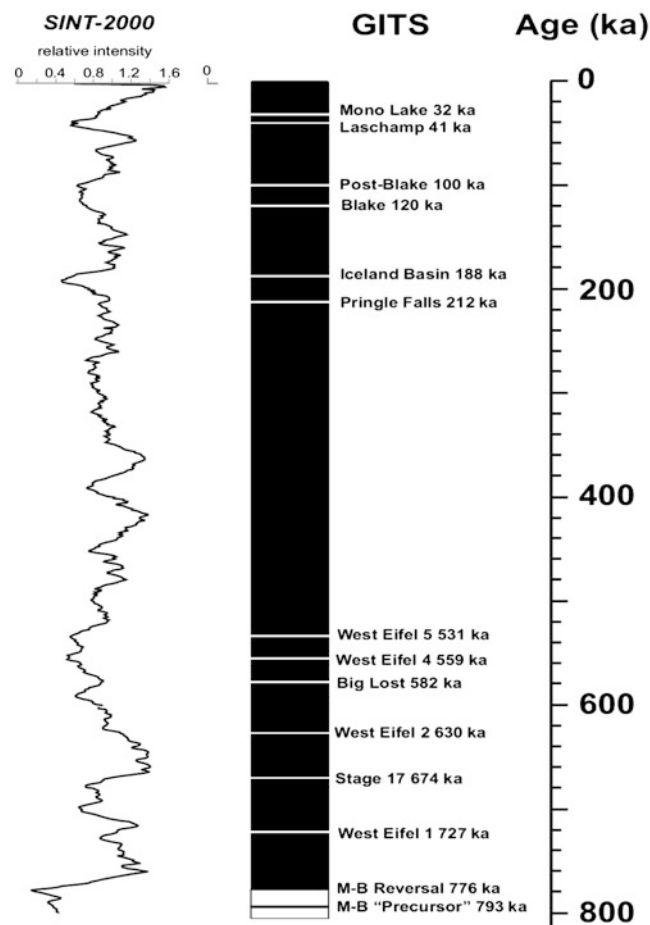


Fig. 2 The geomagnetic instability time scale (*GITS*) for the Brunhes chron. Column at *left* shows the relative paleointensity SINT-2000 stack (Valet et al. 2005). Ages in the *GITS* are from $^{40}\text{Ar}/^{39}\text{Ar}$ dated lava flows and astrochronologically dated Ocean Drilling Project (ODP) cores (Singer et al. 2014 and references therein, figure modified from Singer et al. 2014)

less than 30° on the Earth's surface, as they are not global field features. On the other hand, as features of the geomagnetic field like the Laschamp or Iceland Basin excursions represent full polarity reversals and all adequately defined excursions are characterized by a decrease in intensity (e.g., Laj and Channell 2007), they can be valuable in Quaternary geochronology if used with caution. Nevertheless, their short duration (less than 5 ky, e.g., Laj and Channell 2007) also imposes limitations to their applicability to chronological purposes, as they can be filtered out of sedimentary records (Merril and McFadden 2005).

Archaeomagnetism and Paleosecular Variation

The study of the magnetization found in archaeological objects – and mainly of the TRM recorded in materials which have undergone firing at the time of their fabrication or use – is called archaeomagnetism. Retrieval of the direction of magnetization requires that the studied objects are in situ or their original position is known. Other artifacts may have been fired in an unknown position and only their paleointensity (called archaeointensity) can be determined. Also lava flows whose age is known from historical records can be used for archaeomagnetic studies. When the age of the object or its last firing is known – by methods such as radiocarbon dating, thermoluminescence, and the use of historical records – the archaeomagnetic and archaeointensity data obtained can be incorporated into a master curve for the region where the remanence was acquired (Fig. 3). The establishment of regional archaeomagnetic records needs that individual determinations from

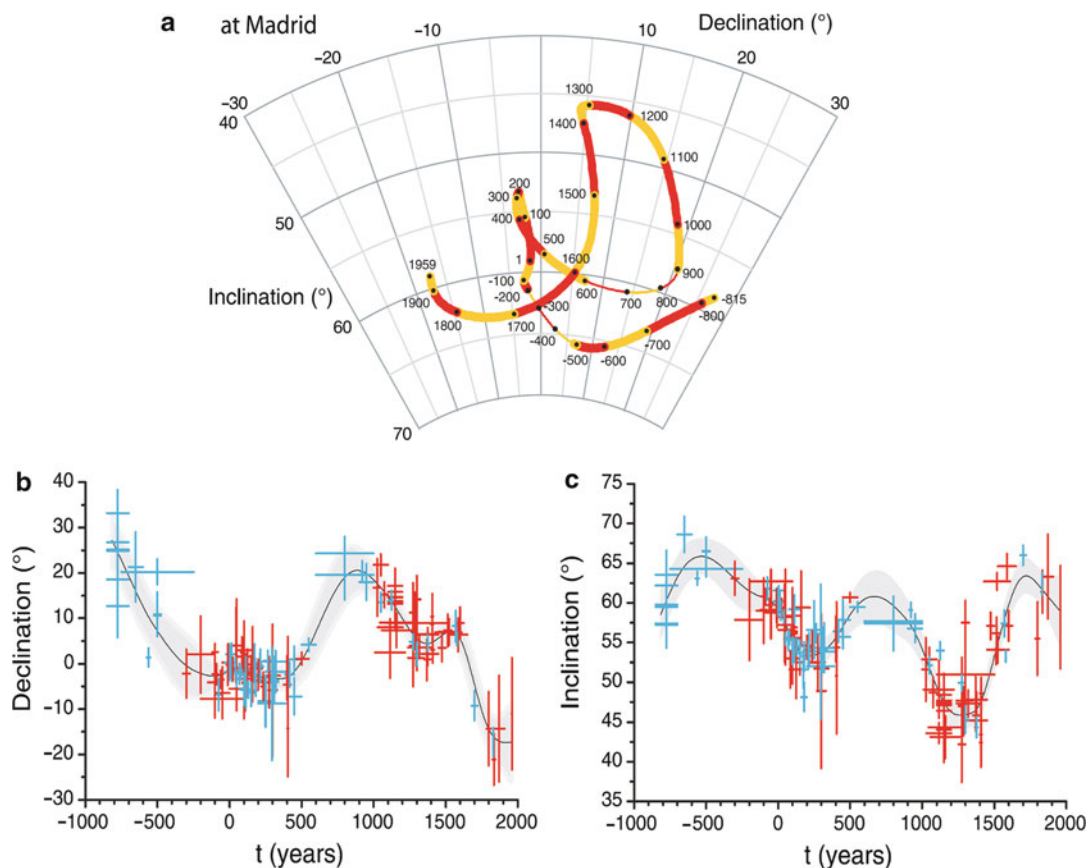


Fig. 3 Secular variation curve for Iberia obtained by Bayesian modeling of data coming from localities less than 900 km from Madrid: (a) stereoplot of declination and inclination, where orange and red indicate century time scales. A thin line indicates curve sectors based on a small number of data, (b) declination versus time, and (c) inclination versus time (Figure from Gómez-Paccard et al. 2006, this figure is reproduced with permission of John Wiley & Sons, Inc.)

different locations are reduced to a common one, following the approximation that the geomagnetic field is described by a tilted dipole (Noël and Batt 1990). Due to the importance of non-dipole field components in secular variation, master curves for directional studies can be only constructed for areas of subcontinental size, of not more than about 1,000 km radius. Spatial variations in intensity are usually modeled using an axial geocentric dipole model of the geomagnetic field. Archaeomagnetic dating is performed by comparing directional and intensity data of an archaeological artifact of unknown age with a reference curve (Fig. 3).

Secular variation that predates magnetic observatories is often referred to as paleosecular variation (PSV). The most suitable material for PSV studies are sediments which can provide a high resolution and a good continuity, like oceanic sediments of continental margins or lake sediments. In PSV studies in lakes, several cores are usually obtained and correlated using physical characteristics of the sediments like magnetic susceptibility or other lithological markers. Age control is provided by varve counting, isotopic dating on organic material, palynology, and identification of tephra levels. Regional declination, inclination, and intensity of PSV master curves can be obtained by stacking of PSV records of several lakes of the same region (e.g., Snowball et al. 2007).

Several global models using spherical harmonic analysis have been constructed using archaeomagnetic data, lava flows, and lake sediment records as input data during the last decade (e.g., Korte and Constable 2009). Specific regional models of secular variation have been developed from archaeomagnetic and sedimentary data, which are fitted to series of mathematical functions (e.g., Pavón-Carrasco et al. 2010). This kind of models allows determining a secular variation curve for a chosen location within the study region.

Magnetic Paleointensity Stratigraphy

The dominantly dipolar nature of geomagnetic paleointensity variations provides a global signal not only during polarity reversals but also within periods of stable polarity. This signal can be used to supply a high-resolution (millennial-scale) time scale for Quaternary chronostratigraphy (e.g., Roberts et al. 2013). Sedimentary sequences allow obtaining continuous records of relative geomagnetic paleointensity variations (Fig. 2). Detailed relative paleointensity stacks now span the entire Quaternary, and some records or stacks of records from rapidly deposited sediments provide millennial-scale chronological resolution (e.g., Roberts et al. 2013 and references therein). Recognition that precisely dated, detailed paleointensity records are coherent on a global scale is leading to the use of relative paleointensity as a means to constrain the chronology of a sedimentary sequence, often termed paleointensity-assisted chronology (e.g., Roberts et al. 2013).

Summary

Direction and strength of the Earth's magnetic field vary with time. The changes produced by the main field, which is generated by magnetohydrodynamic processes in the Earth's liquid iron outer core, display periods of the order of a year to millions of years. Analysis of the remanent magnetization recorded by rocks, sediments, and archaeological materials allows retrieving direction and intensity of the ancient magnetic field which produced the remanence.

In order to be useful as a dating tool, the changes of direction and intensity of the EMF both with time and with location – if variations are of regional character – have to be known. If EMF variation reference curves or data have been obtained and dated with other methods (radiometric dating, fossil record, etc.), they can be compared with the polarity, directional, or intensity record of the studied

geological units or archaeological artifacts to be dated. Magnetic chronology methods and techniques differ, however, according to the age and the time resolution needed.

Cross-References

- ▶ [Archaeomagnetic Dating](#)
- ▶ [Geochronology](#)
- ▶ [Geological Time Scale](#)
- ▶ [Geomagnetism](#)
- ▶ [Magnetic Anomalies](#)
- ▶ [Magnetism, Rock and Mineral](#)
- ▶ [Magnetostatigraphic Dating](#)
- ▶ [Sediments, Marine \(Palaeomagnetism\)](#)
- ▶ [Sediments, Terrestrial \(Palaeomagnetism\)](#)
- ▶ [Volcanic Rocks \(K-Ar/Ar-Ar\)](#)

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Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence

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Definition

Point defects in solids. Any break in the regular pattern of a crystal, due to absence of an atom (vacancy) or to an atom of the crystal in a position out of the regular lattice (interstitial) or an extra atom of different species (impurity).

Luminescence. Energy emission in the form of light as a consequence of absorption of energy of various types: As an example radioluminescence occurs when a crystal emits light after absorption of ionizing radiation. As a general rule luminescence involves electrons that increase their energy level in the absorption (excitation) and return to the original level causing light emission (de-excitation).

Delayed luminescence is a particular type of luminescence occurring when on average there is light emission long after the energy absorption. The most frequently reported delayed luminescence is phosphorescence, caused by transition rules that make scarcely probable the radiative recombination.

Thermoluminescence (TL) is a kind of delayed luminescence in a solid. The excited electrons are “trapped” in defect sites. TL is stimulated by increasing the temperature of the emitting crystal, which causes a higher probability of “detrapping” the electrons, allowing them to recombine at luminescence centers, with light emission.

Optically stimulated luminescence (OSL) is another kind of delayed luminescence in a solid, where detrapping of electrons is caused by light stimulation in place of the heating of TL.

Radiation dosimetry. The measurement of the amount of energy absorbed due to the exposition of a material to ionizing radiation. Delayed luminescences, TL and OSL, are appropriate dosimetric techniques.

Electron spin resonance (ESR). Spectrometric technique which detects unpaired electrons in a material. It is also exploited as a dosimetric and dating technique.

Introduction

Quartz is one of the most abundant minerals in the continental crust of the Earth. It is also industrially synthesized to exploit its properties as an electronic oscillator and is present in many electronic devices for high-frequency clocks.

Like all natural and synthetic materials, quartz contains variable concentrations of defects which can have positive and negative effects. In the case of quartz electronic oscillators, the presence of low concentrations of Al ions, which substitute Si ions, produces an unwanted radiation-induced frequency shift, due to the charge-compensating alkali ions at the Al sites. The same Al defects

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together with other defects are responsible for electronic trapping and luminescence recombination that are very useful for dosimetric purposes: based on these properties, radiation dosimetry and ceramics dating are possible.

To correctly deal with these cases, the probability of detrapping must be considered and the phenomenon generally follows an exponential decay and is temperature dependent: at a fixed temperature the intensity of the emitted light exponentially decreases (McKeever 1985; Martini and Meinardi 1997). In most cases luminescence is due to the presence of lattice defects that are generally involved in the recombination of charge following detrapping from defects of higher energy, regardless of the original energy absorption: the emitted wavelengths are very often the same in the various types of luminescence of a certain material. Looking at delayed luminescences, OSL and TL, further defects are to be considered, specifically the ones responsible for charge trapping.

Quartz Defects

The luminescence properties of quartz defects have been the subject of a large number of studies aimed at understanding the complex mechanisms governing the various luminescence emissions and their modifications as a consequence of irradiation and thermal treatments (Preusser et al. 2009; Lieb and Keinonen 2006).

Many defects, both intrinsic and impurity related, are known to be present or produced in quartz, having been identified through various spectroscopic techniques; however so far the role of these defects in producing luminescence emissions is still under discussion. Although a great number of studies have been carried out on the structure properties of defects in quartz, mainly through ESR measurements (Weil 2000), only tentative correlations between defects and luminescence emissions have been put forth. Many defects are known to be present both in the crystalline (quartz) and in the amorphous (silica) forms of SiO_2 , but the luminescence properties of quartz and silica are largely different (Stevens Kalceff and Phillips 1995). Nonetheless there is agreement on the role of some impurity defects in quartz, particularly the so-called Al centers in being related to the emission dynamics (Halliburton et al. 1981; Martini et al. 2012a).

Some intrinsic or impurity-related defects have been proposed as responsible for the luminescence emissions in quartz, while only few proposals of trapping centers are present in the scientific literature so far. It is to be remembered that it happens often that traps and recombination centers are strongly spatially related and some OSL and TL have been proposed to be of this kind (Itoh et al. 2002; Martini et al. 2009).

Two main kinds of quartz defects are reported as related to its luminescence properties: oxygen vacancies, the most frequently occurring intrinsic defects, and Al centers, an ubiquitous type of impurity center. Besides these defects, other impurities, like Ti, Fe, and Ge ions, give origin to many defects, and Si vacancies are known to be present as a counterpart to oxygen vacancies; they give origin to H_4O_4 centers, where the presence of H^+ ions balances the Si^{4+} missing charge.

Oxygen Vacancies

The simplest type of O vacancy is the diamagnetic center resulting from the removal of an O atom from the otherwise perfect α -quartz, leaving a direct bond between two Si atoms (Feigl et al. 1974).

This “neutral O vacancy” is often considered as the precursor of the paramagnetic E'_1 center, which can be described as a hole trapped at a neutral O vacancy. The resulting defect features an unpaired electron on one of the two Si atoms, while the other Si ion, being positively charged,

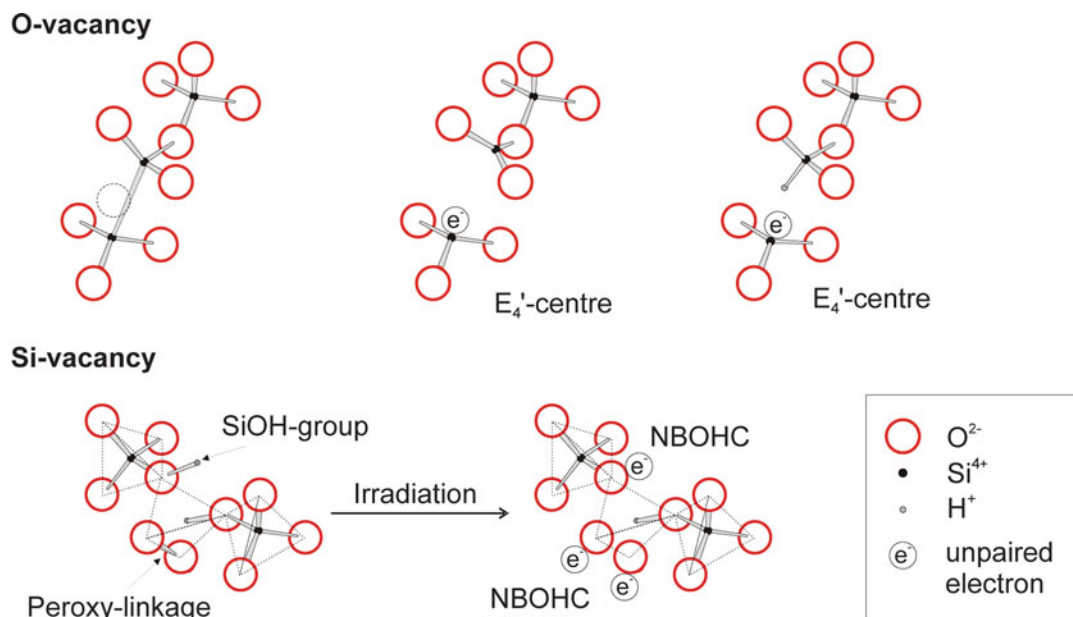


Fig. 1 Intrinsic defect centers in quartz (Taken from Preusser et al. 2009)

moves away from the vacancy into a nearby plane configuration (Fig. 1) (Rudra and Fowler 1987). The neutral O vacancy capturing a hole is often considered as the most likely precursor of the E'_1 ; however, this relationship is controversial and the precursor of E'_1 is still to be identified.

Besides the E'_1 center, E'_2 and E'_4 are known to be present in quartz as modifications of the E'_1 , being related to the presence of H ions (Fowler et al. 1988). A further group of O deficient centers is the E'' . They are very similar to the E' centers, wherein the number of primes denotes how many unpaired electrons a center possesses. Specifically E''_1 , E''_2 , and E''_3 have been reported, characterized by their slightly different ESR signal (Bossoli et al. 1982). They are all quenched by heating the quartz in the temperature range 50–100 °C.

Al Centers

Al^{3+} ion is the main ubiquitous impurity to which many defects are associated. It is present as a substitutional ion for Si^{4+} and is charge compensated by an alkali ion (M^+) or by an H^+ ion, giving rise to $[AlO_4/M^+]^0$, $[AlO_4/H^+]^0$, respectively. When neither M^+ nor H^+ is present near a substitutional Al^{3+} ion, this latter can be charge compensated by a positive hole, giving rise to the $[AlO_4]^0$ center (Halliburton et al. 1981). The three kinds of Al centers and their interrelations are shown in Fig. 2.

Quartz Luminescence, TL and OSL

Many useful results on quartz luminescence come not only from TL and OSL, but also following other types of stimulation, mainly cathode- and radioluminescence. In these cases trapping is not considered and only luminescence centers are investigated.

Three main emissions are known to be present in quartz luminescence: a UV luminescence reported at 330–380 nm; a blue luminescence, generally reported at around 470 nm; and a red luminescence at around 620 nm. It must be noted that the listed emissions (UV, blue and red) are probably composite. This would explain why each of them is often reported at different wavelengths. The blue emission has been shown to be due to the sum of a band at 485 nm (2.53 eV) and

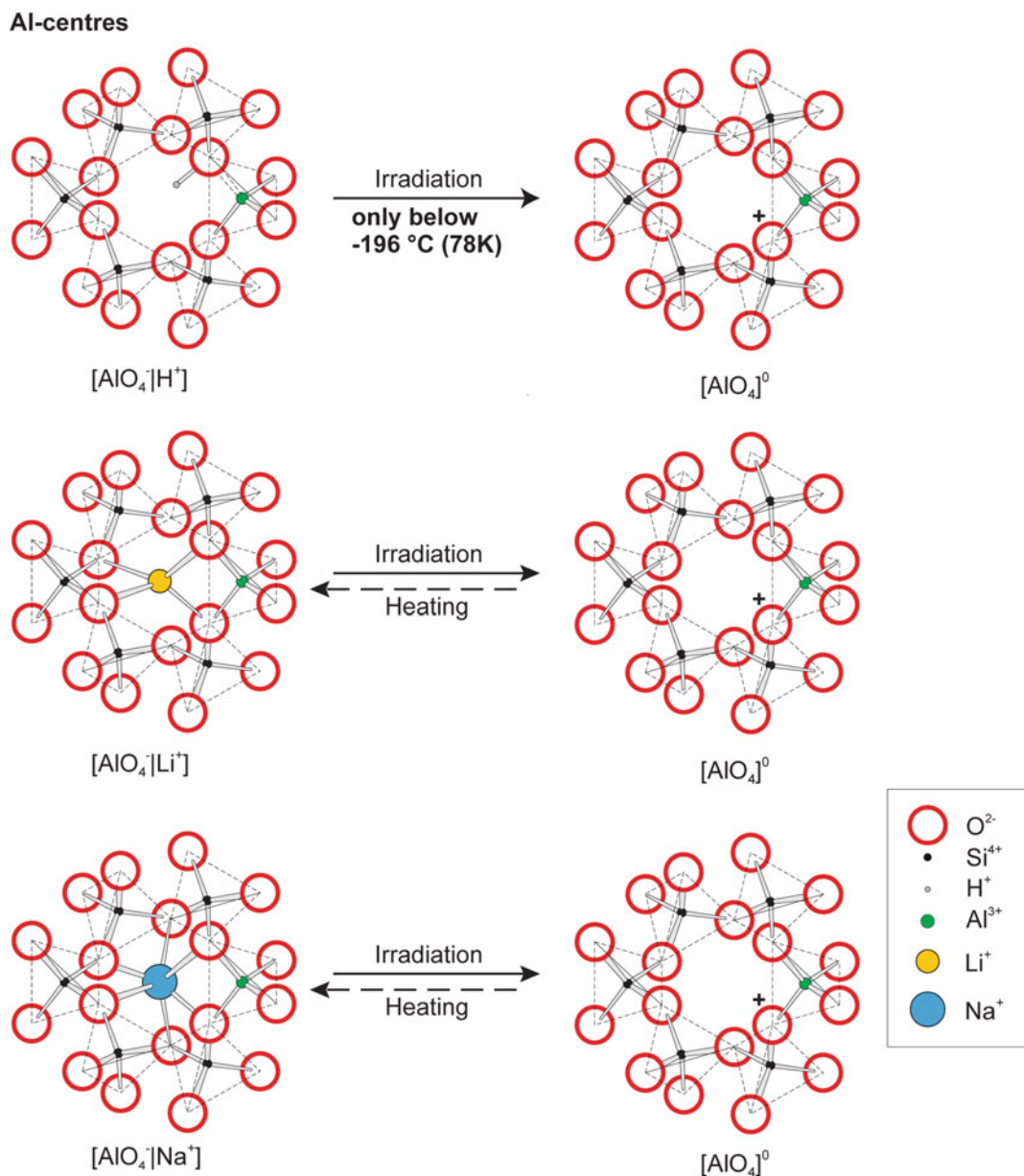


Fig. 2 Al centers in quartz (Taken from Preusser et al. 2009)

a band at 435 nm (2.85 eV). In radioluminescence spectra the first is enhanced by irradiation and the second is quenched by it (Martini et al. 2012b).

A typical TL glow curve of quartz is given by three main glow peaks at around the following temperatures (using a 20°C/s heating rate): 110°C , 220°C , and $325\text{--}375^\circ\text{C}$. The emission wavelength at a given temperature can vary among different types of quartz, but also in some cases different glow peaks in the same specimen emit at the same wavelength.

The 110°C TL peak in an untreated quartz emits in the blue, but after repeated room temperature (RT) irradiation, followed by heating to temperatures in the range $350\text{--}450^\circ\text{C}$, the sensitivity of the quartz crystal greatly increases, even of orders of magnitude: this is the phenomenon known as “pre-dose effect.” Zimmerman (1971) interpreted the increased intensity as the result of an increase in activated luminescence center concentration. It is to be noted that the 110°C TL emission of

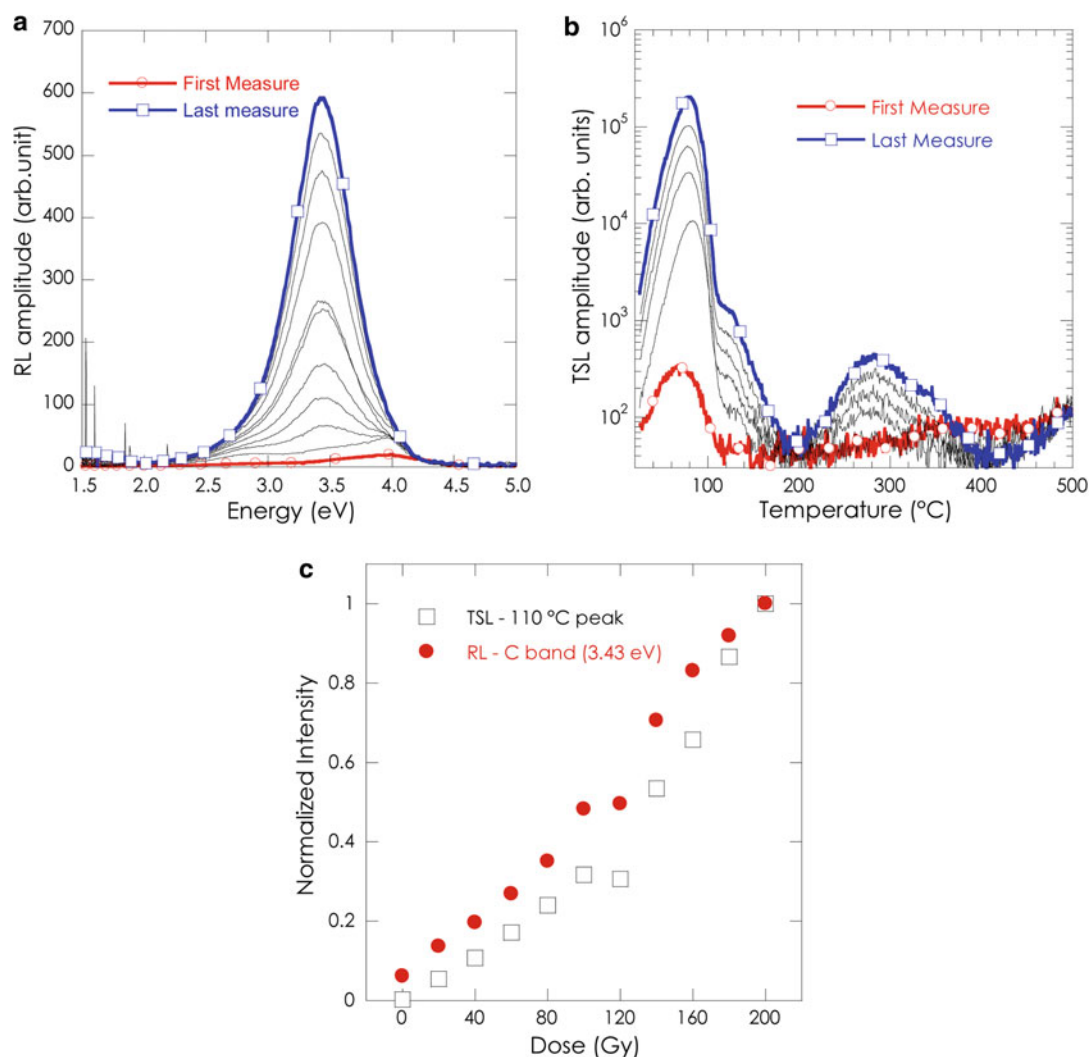


Fig. 3 (a) Sequence of radioluminescence spectra of a natural quartz during irradiation (each spectrum after a dose of 20 Gy), followed by a heating up to 500 °C. (b) Sequence of thermoluminescence glow curves of a natural quartz after irradiation (each spectrum relative to a dose of 20 Gy), followed by a heating up to 500 °C, like in (a). (c) Dose response curve of the 360 nm (3.43 eV) radioluminescence emission band and of the 110 °C thermoluminescence glow peak. The data are normalized to the final value (Taken from Martini et al. 2012b)

a “pre-dosed” quartz is in the UV, at 360 nm; see Fig. 3 (Martini et al. 2012b). OSL emits in the UV as well (Huntley et al. 1996; Martini and Galli 2007), and this was supported by evidence of a pre-dose effect for the OSL signal (Stoneham and Stokes 1991; Koul and Chougankar 2007).

OSL, as well as TL, is also seen to greatly enhance its sensitivity as a consequence of high temperature annealing (Poolton et al. 2000; Schilles et al. 2001; Chen et al. 2001; Lai et al. 2008). This effect is proposed to be related to the variation of concentration of E’₁ centers that may act as non-radiative centers competing in the recombination process (Poolton et al. 2000).

The emission wavelength of the main dosimetric TL peak at 375 °C is strongly dependent on the origin of quartz: some quartzes have a dominant blue emissions, others emit in the red (Shimizu et al. 2006).

It is to be noted that the most commonly used filters to detect TL are centered at around 400 nm, with high efficiency for detecting the blue emissions at about 470 nm, while the red TL at about 640 nm is effectively excluded.

In most quartz a further glow peak is seen at 325 °C. This glow peak has been related to the 110 °C glow peak and to OSL (Kaylor et al. 1995; Wintle and Murray 1997). It has been seen to have the same emission as the OSL and the 110 °C peak, in the range 380–420 nm.

Recombination Models

So far it is not possible to definitely assign each emission to a specific center; however some proposals find a good deal of support. There is agreement on the fundamental role of Al centers in participating in the luminescence of quartz. In untreated quartz, Al is known to be present mainly as charge compensated by an alkali ion, generally Li^+ . Irradiation detaches Li^+ which is then free to move along the channels parallel to the crystallographic c-axis. The effect is the transformation of $[\text{AlO}_4/\text{Li}^+]^0$ to $[\text{AlO}_4/\text{H}^+]^0$ or to $[\text{AlO}_4]^0$ centers, depending on how many H^+ ions are available.

By making specific electro-diffusion treatments (“sweeping”), it is possible to modify the concentration of alkali ions in quartz; if this sweeping is made in air at RT, alkali ions are substituted by H^+ at the Al^{3+} sites. By sweeping out in vacuum at high temperature, Martini et al. (1995) could eliminate from quartz crystals both $[\text{AlO}_4/\text{Li}^+]^0$ and $[\text{AlO}_4/\text{H}^+]^0$, replacing most of them with $[\text{AlO}_4]^0$ centers. They suggested that the 380 nm emission is the result of recombination at $[\text{AlO}_4]^0$ centers, contrary to Yang and McKeever (1990) who related the enhancement of the intensity of the 380 nm emission to changes in ESR active centers, assigning the emission to electron–hole recombination at $[\text{H}_3\text{O}_4]^0$ centers. $[\text{AlO}_4]^0$ has been also proposed as the defect responsible for the blue TL at 470 nm (Woda et al. 2002; Yang and McKeever 1990).

Sweeping turned out to be extremely useful in the study of defects in quartz. Jani et al. (1983) reported a correlation between the growth of the E'_1 center and the decay of the $[\text{AlO}_4]^0$ center and observed that sweeping out the alkali ions strongly reduces the intensity of the E'_1 ESR signal. Poolton et al. (2000) suggested that E'_1 may act as a non-radiative center competing in OSL with the $[\text{AlO}_4]^0$ recombination center.

Quartz Types and Luminescence

Quartzes of different origin present different luminescence emissions: volcanic quartz generally emits in the red (Westway 2009), while slow solidification in plutonic rocks results in strong blue emission (Hashimoto 2008). Hydrothermal quartz also emits at ~480 nm, but the emission has been reported as weak (Rink et al. 1993; Rendell et al. 1994). Shimizu et al. (2006) detected a single emission peak in the red (~630 nm) for a sample of volcanic quartz.

It should be noted however that red emission has been detected in silica, but never in synthetic quartz. Its presence in volcanic quartz could be related to the amorphous inclusions probably present in this kind of natural quartz. Rink et al. (1993) also noticed a large red intensity in volcanic quartz and suggested an assignment to defect clusters.

Conclusions

Many studies on the TL and OSL emissions in quartz provided evidence related to the defects involved in the radiative recombinations, even if definite assignments of each emission to a specific center are still lacking. The main emissions are known to be in the UV (330–380 nm), in the blue at around 470 nm, and in the red at around 620 nm. Precise measurements are clarifying that these emissions are indeed composite, making it more difficult to correctly follow their behavior as a function of irradiation and thermal treatments. As a consequence the assignments proposed so far

are rather tentative, and a systematic definition of luminescence emissions correlated with defect dynamics must be reached as a first step to the assignment-specific roles to defects.

Nonetheless an important and complex role of Al centers in participating in charge recombination can definitely be concluded, but also that migrations by alkali and hydrogen ions promoted by irradiation and/or heating surely play an essential part.

At the same time, the role of oxygen vacancies in indirectly participating in the radiative recombination is clear.

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Dendrochronology: Surficial Processes

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Synonyms

[Dendrogeomorphology](#); [Geomorphology](#); [Earth-surface process](#)

Definitions

Dendrochronology (tree-ring dating): scientific method of dating based on the analysis of patterns of tree rings, also known as growth rings. Dendrochronology can date the time at which gymnosperms and some angiosperms (woody dicotyledonous) were formed tree rings to the exact calendar year.

Surficial processes: processes on the earth surface that shape or have shaped landforms.

Dendrogeomorphology: scientific method to date earth-surface processes in terms of frequency, magnitude, and spatial pattern using the growth-ring series of affected trees.

Introduction

The significant contribution of tree rings to document earth-surface processes lies in their capacity to both preserve evidence of past geomorphic activity and provide critical information on their dating with annual or sub-annual resolution. In many climates, the tree-ring record may represent the most valuable and precise natural archive for the reconstruction and understanding of past and ongoing earth-surface processes during the last several hundred years. As many geomorphic processes are significant natural hazards, understanding their distribution, timing, and controls provides valuable information that can assist in the development of mitigation and defense against these hazards and their effects on society.

This contribution provides an overview of tree-ring-based reconstructions of surficial processes resulting from different geomorphic agents. It outlines the impact of earth-surface processes on tree morphology and wood anatomy and clarifies the approaches used for tree-ring reconstruction of past activity of earth-surface processes. This entry also illustrates the breadth and diverse applications of contemporary dendrogeomorphology and underlines the growing potential to expand these studies, possibly leading to the establishment of a range of techniques and approaches that may become standard practice in the analysis of specific hazards.

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What Surficial Processes Can Be Analyzed with Tree Rings?

Dendrogeomorphology has been used in the analysis and reconstruction of a wide range of surficial processes. Some of the earliest applications of dendrochronological research to earth-surface processes utilized roots rather than stem samples to study **erosion processes**. In the 1960s, LaMarche (1968) used tree roots exposed by surface lowering as an indicator of ground surface at the time of germination of 5,000-year-old *Pinus aristata* Engelm. in the White Mountains, California. Corona et al. (2011) focus on areal denudation in marly badlands in the French Alps and illustrate limitations and possible caveats of past approaches using growth rings of roots to reconstruct erosion rates. Stoffel et al. (2012) reconstructed channel wall retreat related to flash floods in the Patagonian Andes of Argentina, and Fantucci (2007) utilized roots to analyze shore erosion in Central Italy.

After the pioneering studies of Hupp (1984) conducted on Mount Shasta (California), tree-ring records were used by Strunk (1991) to reconstruct **debris-flow activity** in the Italian Dolomites. More recently, the frequency and spatial patterns (i.e., lateral spread and extent of flows) have been analyzed in the Swiss Alps (Stoffel et al. 2008; Bollschweiler and Stoffel 2010), including dendrogeomorphic work on frequency-magnitude relations of debris flows (Stoffel 2010) and precipitation thresholds (Schneuwly-Bollschweiler and Stoffel 2012).

Dendrogeomorphic analyses of **landslides** were realized primarily in Canada (Bégin and Fillion 1985) and the French Alps (Braam et al. 1987; Lopez Saez et al. 2013) to document spatial patterns of activity, reactivations, and rainfall patterns triggering landslides. In the first study in the subtropics, Paolini et al. (2005) used suppression-release patterns and inception of *Alnus acuminata* Kunth. trees to date a number of landslides in Argentina.

The occurrence of **snow avalanches** has quite frequently been analyzed with tree rings over the last four decades, beginning with Schaerer's (1972) publication on vegetation in avalanche terrain in British Columbia (Canada). For a long time, tree-ring-based analysis of snow avalanche activity was almost exclusively used in North America (Butler 1979; Germain et al. 2009). Work in the European Alps started in the early 2000s with a focus on runout distances and triggering weather conditions (Stoffel et al. 2006a; Corona et al. 2012).

The analysis of growth rings has also been used in paleohydrology. The first studies linking **fluvial processes** and botanical evidence go back to the 1960s (Sigafos 1964). Later on, a broad array of flood signatures have been defined to date paleofloods (St. George and Nielsen 2000). More recently, scarred trees have been used to estimate flood discharge (Ballesteros et al. 2011) and to analyze flood frequency distributions (Ballesteros et al. 2013).

Surprisingly, and despite the potential of dendrogeomorphic methods, rockfall activity has only rarely been studied with tree rings (Stoffel 2006). The first studies analyzing the seasonality, frequency, and spatial patterns of **rockfalls** using tree rings were only very recently realized by Stoffel et al. (2005) and provided a reliable basis for the analysis of rockfall risks and the accuracy assessment of rockfall models (Stoffel et al. 2006b).

Recent comprehensive discussions of dendroglaciology can be found in Koch (2009). The first, simplest, applications involve determining the inception date of the oldest tree growing on a moraine or other surface to provide a minimum age for the feature or, more rarely, estimates of the rates of glacier recession or succession. In many areas around the world, the glacier advances of the last few centuries were more extensive than earlier Holocene events, and significant dendroglaciological work has been done using recently exposed stumps or logs in glacier forefields to estimate the dates of earlier events or ice-free periods, providing the tree-ring records can be cross-dated against reference chronologies. However only kill dates from in situ materials provide

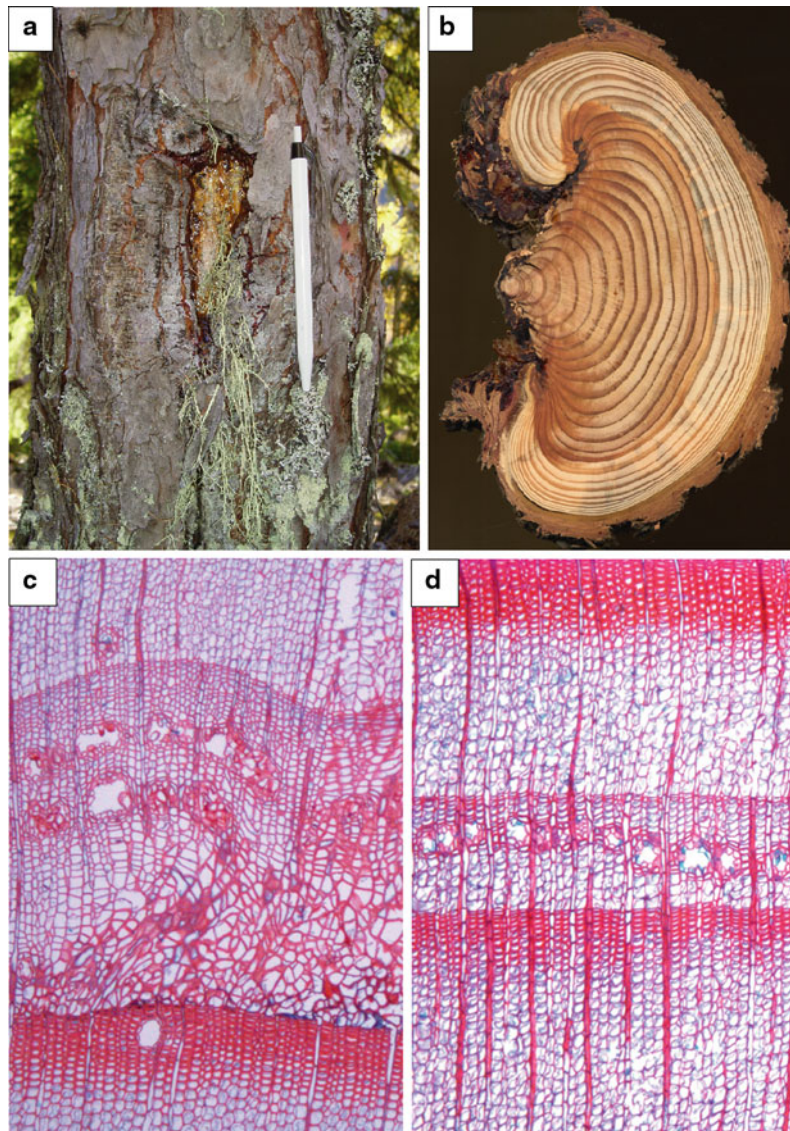


Fig. 1 Injuries in *Larix decidua* Mill: (a) injured stem (b) cross section with overgrowth starting from the lateral edges of the injury. (c) Callus tissue as observed in the overgrowing cell layers bordering the injury. (d) Tangential row of traumatic resin ducts migrating from earlywood toward later portions of the tree ring with increasing distance from the wound

the precise location of the glacier when the tree was killed, detrital material having been killed some unknown distance up-glacier cannot yield such data.

Tree Reactions to Earth-Surface Processes

Apart from the site-specific information common to many trees at any site (e.g., genetic information, age, or climatic conditions), individual trees also record the effects of mechanical disturbance caused by external processes. Trees can be injured, suffer breakage of their crown or branches, and have their stems tilted, partially buried, or their roots exposed. Evidence of these events can be recorded in the tree-ring series of affected trees (Fig. 1). The analysis of geomorphic processes

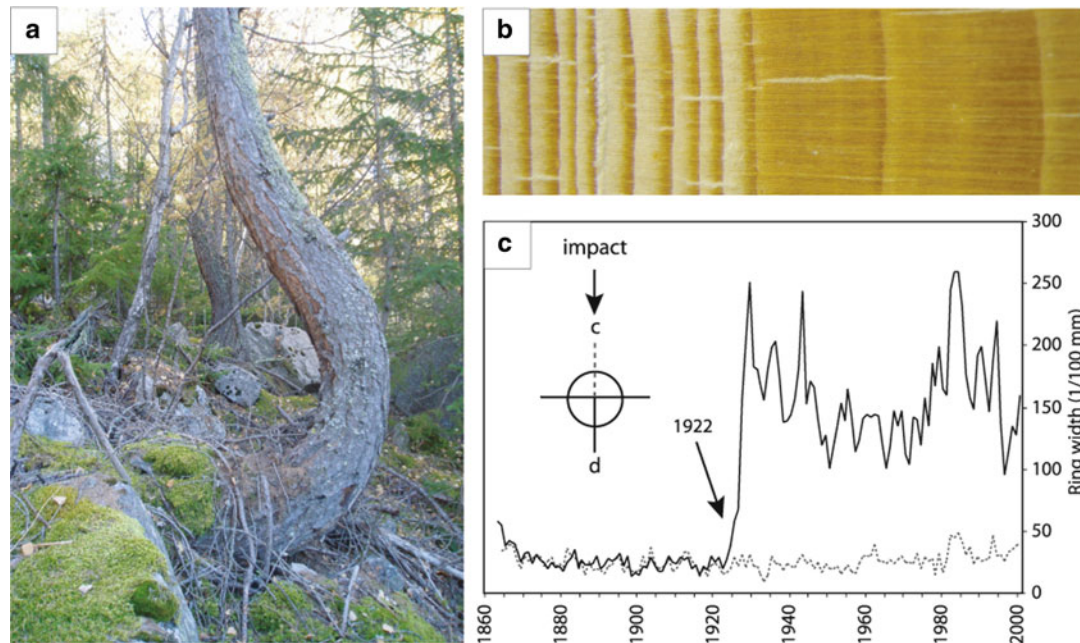


Fig. 2 (a) Tree morphology and (b) cross sections of a tilted *Larix decidua* Mill. (c) Increment curves of a *Picea abies* (L.) Karst. tree tilted by a debris flow in 1922

through the study of growth anomalies in tree rings is called dendrogeomorphology (Alestalo 1971). Dendrogeomorphic research is normally based on the “process–event–response” concept as defined by Shroder (1978) where the “process” is represented by any geomorphic agent, e.g., debris flows, snow avalanches, or rockfall (Stoffel et al. 2010). Individual geomorphic “events” that affect the tree may result in a range of growth “responses.” These “events” and associated “responses” are illustrated in the following paragraphs.

Mechanical disturbance and **wounding** are very common features in trees affected by geomorphic processes. When impact locally destroys the vascular cambium, increment cell formation is disrupted and new cell formation ceases in the injured segment of the tree (Fig. 1a, b). To minimize rot and insect attacks after damage, the injured tree will compartmentalize the wound and start production of chaotic callus tissue (callus tissue = mass of unorganized parenchyma cells in plant tissues formed after wounding; Fig. 1c) at the edges of the injury (Shigo 1984). The extent of wound healing greatly depends on the annual increment rate, the age of the tree, and on the size of the scar. After injury, tangential rows of traumatic resin ducts (or TRD = compact and continuous rows of resin canals formed as a result of cambium damage. TRD are an excellent proxy to date mass movement-induced mechanical impact in trees; Fig. 1d) are produced in the developing secondary xylem of certain conifer species, e.g., *Larix* sp., *Picea* sp., *Pseudotsuga* sp., or *Abies* sp. (Stoffel 2008). They extend tangentially and axially from the injury (Bollschweiler et al. 2008; Schneuwly et al. 2009). When wounding occurs during the vegetation period of the tree, resin production will start a few days after the event and ducts emerge within 3 weeks after the disturbing event. Therefore, when analyzing cross sections, the intra-seasonal position of the first series of TRD can be used to reconstruct previous events with monthly precision (Stoffel et al. 2008; Stoffel and Hitz 2008). In broad-leaved species, cambial damage will initiate various anatomical responses, among those a reduction vessel sizes (Arbellay et al. 2010, 2012).

Inclination of the stem results from the sudden pressure induced by geomorphic processes directly, by the associated deposition of material (e.g., avalanche snow, debris-flow material), or

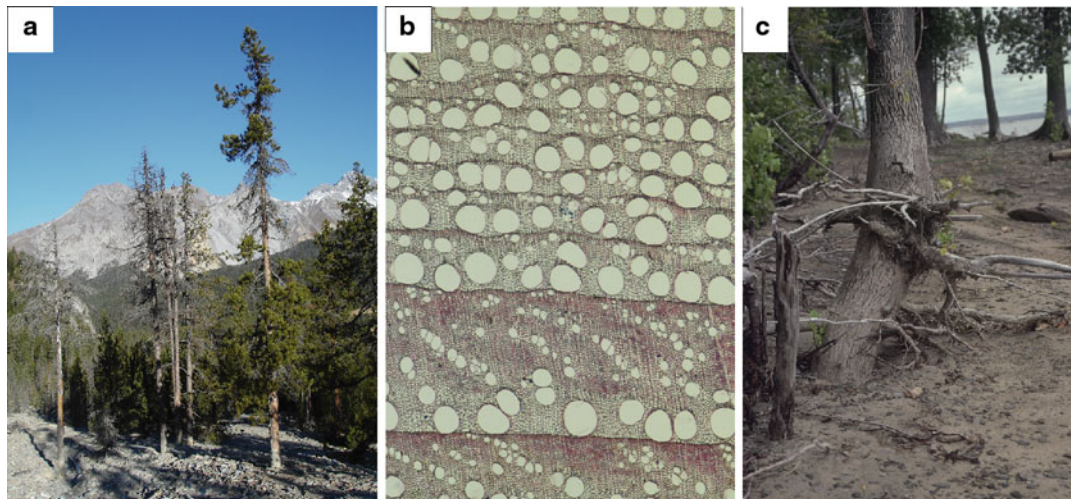


Fig. 3 (a) Sedimentation and subsequent die-off of trees after sedimentation. (b) Microsection showing an abrupt growth decrease in *Castanea sativa* Mill. (c) Several levels of adventitious roots in *Populus deltoides* Bartr. ex Marsh

by the slow but ongoing destabilization of a tree through landslide activity or erosion (Lundström et al. 2009). **Tilted trees** (Fig. 2a) are common in many areas affected by geomorphic processes and have therefore been used in many dendrogeomorphic studies to date previous events (Braam et al. 1987). Subsequent growth in the trunk of a tilted tree will attempt to restore its vertical position, and the reaction will be most clearly visible in that segment of the tree to which the center of gravity has been moved to through the inclination of the stem axis. In the tree-ring record, eccentric growth (and related reaction wood; Fig. 2b, c) will be visible after a tilting event and thus allow accurate dating of the disturbance. In coniferous trees, compression wood will be produced on the underside of the trunk. Individual rings will be considerably larger and slightly darker in appearance as compared to the upslope side. The difference in color results from much thicker and rounded cell walls of early- and latewood tracheids (Timell 1986). Multiple tilting events in the same stem may be recognized by changes in the amount, color, or orientation of reaction wood series in the ring series. In contrast, stem tilting in broad-leaved trees leads to the formation of tension wood on the upper side facing the tilting agent. Broad-leaved trees also react upon tilting with ultrastructural modifications that are only visible when studied on microsections (Pilate et al. 2004). In addition to the formation of different types of reaction wood, trees may also respond with reduced growth after tilting (Mayer et al. 2010).

Debris flows, floods, landslides, or “dirty” snow avalanches may **bury trees** by depositing material around their stem base (Fig. 3a). Growth in these trees will normally be reduced as the supply of water and nutrients will be temporarily disrupted or at least limited (Fig. 3b; Kogelnig et al. 2013). If stem burial exceeds a certain threshold, trees will die from a shortage in water and nutrient supply. According to case-study results from the Italian Dolomites (Strunk 1991), *Picea abies* (L.) Karst. may tolerate a maximum burial depth of 1.6–1.9 m in environments dominated by fine-grained debris flows composed of calcareous material. Occasionally, buried trees produce adventitious roots close to the new ground surface. As adventitious roots are typically formed in the first years after burial, the moment of root sprouting can be used to derive an approximate date for the sedimentation processes (Strunk 1991).

Bouncing rocks and boulders, debris in flowing water, debris flows and lahars, or the windblast of snow avalanches may cause **decapitation of trees** or the removal of branches. The loss of the crown or branches is more common in bigger trees, when stems have lost their flexibility. Apex

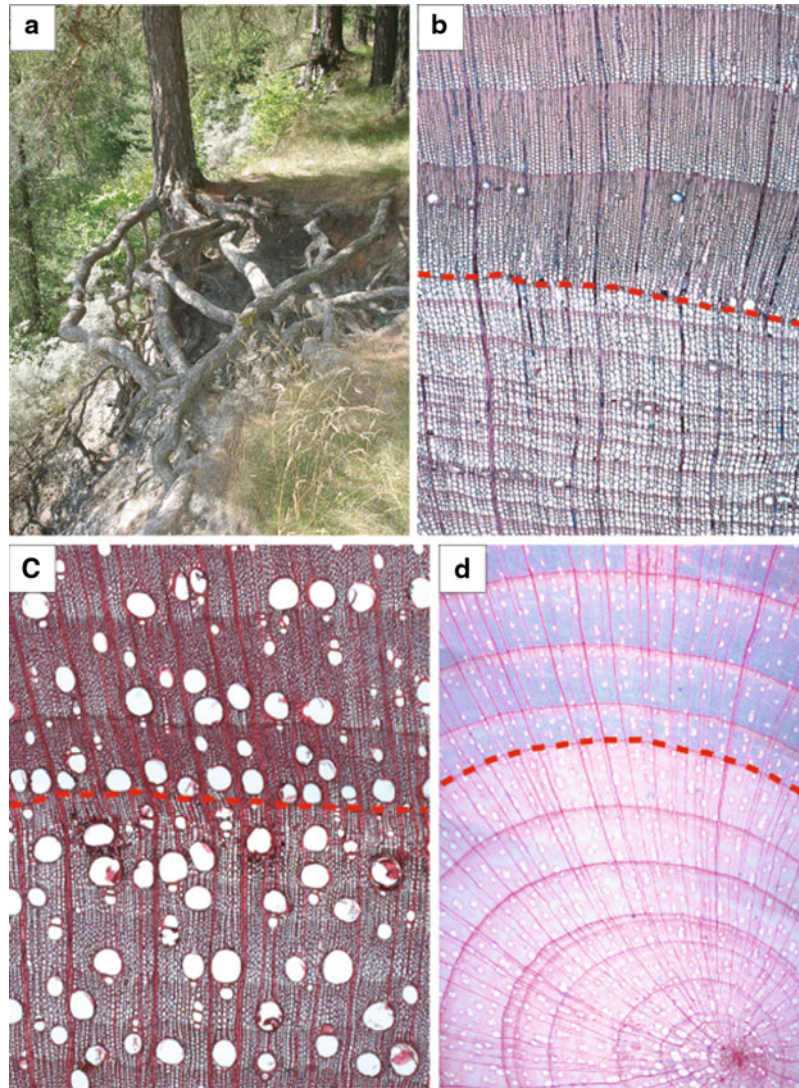


Fig. 4 (a) Exposed roots of *Pinus sylvestris* L. (b) In *Abies alba* Mill., larger increment rings with distinct latewood are formed after sudden exposure (dashed red line). (c) Following sudden exposure, the arrangement of vessels in *Fraxinus excelsior* L. changes from diffuse porous to ring porous. (d) In addition to cell changes, tension wood is formed in this root of *Acer pseudoplatanus* L.

(apex = uppermost part or growing tip of a plant) loss has also been observed as a result of rockfall impacts close to the ground level. In such cases, the sinusoidal propagation of shockwaves in the stem results in the break-off of the crown. This phenomenon has been described as whiplash or a “hula-hoop” effect (Lundström et al. 2009). Trees react upon decapitation or branch loss with distinct radial growth suppression. One or several lateral branches will form a “leader” that replaces the broken crown, resulting in the tree morphology called “candelabra” growth (Butler and Malanson 1985).

Erosional processes and the (partial) denudation of roots may generate different growth reactions, both in the stem and in the exposed roots (Fig. 4a). The type and intensity of the reaction(s) will depend on the nature of the erosive event, which may be instantaneous or progressive and gradual. If several roots are completely denuded during a sudden erosive event (e.g., debris flow, lahar, flood, or landslide), they are no longer able to fulfill their primary functions

and quickly die. The tree subsequently suffers from a shortage of water and nutrient supply, resulting in suppressed tree growth and the formation of narrow rings in the stem (LaMarche 1968). In cases where only part of a root is exposed and its outer end remains in the ground, the root will continue to grow and fulfill its functions. In the exposed root, however, anatomical changes will occur and individual growth rings similar to those in the stem or branches will be formed (Fig. 4b, d). The localization of this change in the tree-ring series may allow determination of the moment of exposure (Corona et al. 2011). The continuous slow exposure of roots is usually caused by gradual processes and relatively low denudation rates, e.g., by overland flow; the slow opening of cracks in soils (e.g., soil creep, landslides) and in disintegrated bedrock, along rivers, streams, lakes, and oceans (floods, shore erosion); as well as with faulting activity and displacements in relation to earthquake activity (Jacoby et al. 1988, 1992). Provided that the roots are gradually exposed with time, it is also possible to determine the erosion rates in such cases (Stoffel et al. 2013a).

Geomorphic processes can **eliminate trees** along channels or couloirs (couloir = French for “passage” or “corridor,” used to refer to a narrow gully with a steep gradient in a mountainous terrain) through uprooting and stem breakage and leave neighboring trees intact. This phenomenon can be observed with, e.g., rockfalls, debris flows, lahars, extreme floods, landslides, or snow avalanches. The uninjured survivor trees have less competition, more light, nutrients, and/or water. As a consequence, they may start to produce larger increment rings. However, observations indicate that this growth release in survivor trees can be delayed and therefore this reaction cannot always be used to date past destructive events with yearly precision. Nevertheless, the growth release in survivor trees can corroborate the dating of events that have been identified from evidence in other trees at the same site, e.g., from scars, tilted stems, etc. (Stoffel and Corona *in press*).

Many different earth-surface processes can eliminate surface vegetation including entire forest stands, leaving no direct dendrogeomorphic evidence. In such cases, **germination ages of trees growing on bare surfaces** can be used to estimate the time of creation of new landforms and the disturbance event. This approach provides a minimum age for that surface and has frequently been used to date landforms or assess the minimum time elapsed since the last devastating event in snow avalanche couloirs, debris-flow channels, or floodplains (Sigafos 1964; Pierson 2007). It involves estimating the time between the exposure of the surface and the germination of the first surviving seedling on that surface. This “ecesis” estimate varies with the environment, substrate, available seed sources, and several other factors. Problems of ecesis determination have been extensively discussed in studies that attempt to date the formation of glacier moraines (McCarthy and Luckman 1993) where ecesis estimates may vary from a few years to several decades.

Field Approach and Sampling Design

The types of damage to trees described in the preceding section may result from a wide variety of earth-surface processes. Linkage between the damage and the causative process depends on a critical evaluation of the sampling site. In many cases, investigations are undertaken with a specific context where the process or processes involved are known and appropriate sampling methods and sampling design may be applied. These vary considerably with the nature of the process or investigation and are best discussed in the specific context of individual processes, e.g., the sampling network needed to define past earthquake activity may be very different from that required to reconstruct the history of snow avalanches and debris flows on a large debris cone.

At an individual site the choice of sampling design and selection of the trees to be sampled will depend on the purpose of the investigation and the processes or hazards being sampled. The sampled area and number of trees sampled may be very small and specific (e.g., on a small landslide) or may involve systematic sampling of a larger area (e.g., within a large runout zone of a snow avalanche) or target individual trees damaged at the margins of an event. As a rule of thumb, processes that tend to spread considerably will likely leave larger spatial footprints and will thus be visible in a larger number of trees. In the case of landslides, a sample size of 50 trees seems sufficient, a slightly larger sample size (100 trees) appears appropriate for snow avalanches, and at least 150 trees are needed to characterize debris flows appropriately (Stoffel et al. 2013b). The sample size in rockfall studies will depend on the size of the study site, stand density, and mean rock sizes (Trappmann et al. [in press](#)). The choice of the individual trees sampled is based on an inspection of the stem and on the location of the trees with relation to the processes studied.

The tree-ring record of growth disturbances created by past events is analyzed with cross sections, wedges, or increment cores. Cross sections or wedges are normally taken at the location of the growth disturbance and provide an excellent and very complete insight into the tree's history. However, in many locations (e.g., protection forests, National Parks), felling may be prohibited or ill-advised for aesthetic or safety reasons. Most tree-ring studies thus use cores extracted with an increment borer. The nature of visible growth defects observed in the tree's morphology will influence sampling height, sampling directions, and minimum number of samples to be taken per tree.

In trees with visible **scars**, previous geomorphic events are most easily dated through the destructive sampling of trees and the preparation of cross sections taken at the location where the injury is largest. This approach will facilitate an accurate and intra-seasonal identification of the onset of **callus tissue** (and **TRD**) formation and therefore allows a reconstruction of the impacting event with very high temporal resolution. Alternatively, wedges can be sawn from the overgrowing callus and an increment core extracted from the side opposite to the wound (Arbellay et al. 2010).

Tilted stems are usually analyzed with at least two increment cores extracted per tree, one in the direction of the tilting and the other on the opposite side of the trunk. The reaction wood will be visible on the tilted side in conifer trees (= compression wood) and on the side opposite to the tilting direction in broad-leaved trees (= tension wood). Individual cores are best extracted at the location where tilting is strongest based on an outer inspection of the tree morphology. However, in situations where multiple tilting events may vary in direction, e.g., in snow avalanche tracks, additional cores, transverse to the downslope direction, may be needed to develop a more complete record.

In the case of **buried stem bases**, the sampling of two increment cores in opposite directions (ideally from the upslope and the downslope side) will normally allow accurate reconstruction of the event that has led to the sedimentation of material around the stem's base. It is best to sample these trees as close to ground level as possible (ca. 20–40 cm) to extract a maximum number of tree rings and obtain maximum information. However, the influence of roots should be avoided.

The analysis of **exposed roots** is normally based on cross sections, as they regularly show partially or completely missing rings. The position of samples needs to be carefully noted with respect to the ground surface or the non-eroded parts of the root. These samples are essential for the understanding and interpretation of continuous erosion processes and the determination of denudation rates (Stoffel et al. 2013a).

The **germination of trees** on new landforms is best determined by counting the annual growth rings in increment cores taken from the root crown level (root crown = also known as root collar or root neck; part of a root system from which a stem arises and where vascular changes between the

stem and the roots occur). However, branches, obstacles, and rot may sometimes require sampling positions higher up on the stem. In these cases, an age correction factor needs to be added to compensate for the time a tree takes to grow to sampling height. A simple height-age correction can be achieved by dividing the tree height by the number of tree rings to get an average rate for the yearly apical increment.

In some cases a reference tree-ring chronology may need to be developed from a nearby forest stand to assist in cross-dating of trees at the sampled site to verify the age assignment of rings. Adequate sample size varies between species and also depends on the strength of the common signal. In general, 20–30 trees is a useful guide for most species to minimize the potential influence of geomorphic processes and hidden growth disturbances.

Sample Analysis and Interpretation

Ring widths of the disturbed samples may also be measured and the series compared graphically or statistically with the reference chronology. These tools also allow for an assessment of cross-dating accuracy between ring-width series of individual disturbed trees and the reference chronology. Once all tree-ring series are checked, individual growth curves may be analyzed visually to identify the tree's reactions to geomorphic processes, e.g., the initiation of abrupt growth reduction or releases. In addition, the microscopic appearance of the cells may be investigated to yield further evidence of disturbance. Other features, e.g., callus tissue overgrowing scars or the presence of TRD formed following cambium damage, can only be identified through a visual inspection of the cores and cross sections. All growth reactions identified in the samples are noted in order to identify disturbance events. Except for processes with limited volumes (e.g., single rocks or boulders involved in rockfalls), one growth disturbance identified in a single tree is not considered sufficient evidence to identify an event, and therefore the identification of events needs to be based on quantitative or semiquantitative thresholds (Stoffel and Bollschweiler 2008; Stoffel and Corona [in press](#)).

Synopsis

The initial employment of tree rings in geomorphic studies was simply as a dating tool and rarely exploited other environmental information and records of damage contained within the tree. However, these unique, annually resolved, tree-ring records preserve valuable archives of past earth-surface processes on timescales of decades to centuries. As many of these processes are significant natural hazards, understanding their distribution, timing, and controls provides valuable information that can assist in the prediction, mitigation, and defense against these hazards and their effects on society. This entry provides many illustrations of these themes, demonstrating the application of tree rings to studies of snow avalanches, rockfalls, landslides, floods, earthquakes, wildfires, and several other processes. It illustrates the breadth and diverse applications of contemporary dendrogeomorphology and underlines the growing potential to expand dendrogeomorphic research, possibly leading to the establishment of a range of techniques and approaches that may become standard practice in the analysis and understanding of earth-surface processes and related natural hazards in the future.

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Polymerase Chain Reaction DNA Amplification

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Definition

Polymerase chain reaction (PCR) is a method of amplifying DNA from biological samples. This makes it possible to determine the DNA sequence, using techniques such as Sanger sequencing.

Most genetic analyses involve the study of DNA sequences. To obtain these data, the target DNA needs to be amplified so that it can be distinguished from the rest of the DNA present in a biological sample. PCR is a technique that is routinely used to amplify DNA (Mullis et al. 1986; Mullis and Faloona 1987).

PCR requires the design of short DNA fragments (primers) with sequences that match the regions flanking the genetic marker being targeted (Fig. 1). These are added to a mixture of DNA (extracted from the biological sample), a DNA-replicating enzyme (polymerase), basic units for building new DNA molecules (dNTPs), and several other reagents. This mixture is subjected to a cycle of temperature changes. First, high temperature causes DNA to unwind and its two strands to separate (denaturation). Then hydrogen bonding causes the primers to attach specifically to matching sections of DNA (annealing). In the final part of the cycle, polymerase uses the original DNA strand as a template for copying the nucleotide sequence and attaches dNTPs to the new strand that has been started by the primers (elongation). This process is repeated a large number of times, with each cycle causing the number of target DNA molecules to double. Using PCR, the amount of target DNA can be massively increased, allowing the DNA sequence to be determined using other techniques.

Cross-References

► [Gene Sequencing](#)

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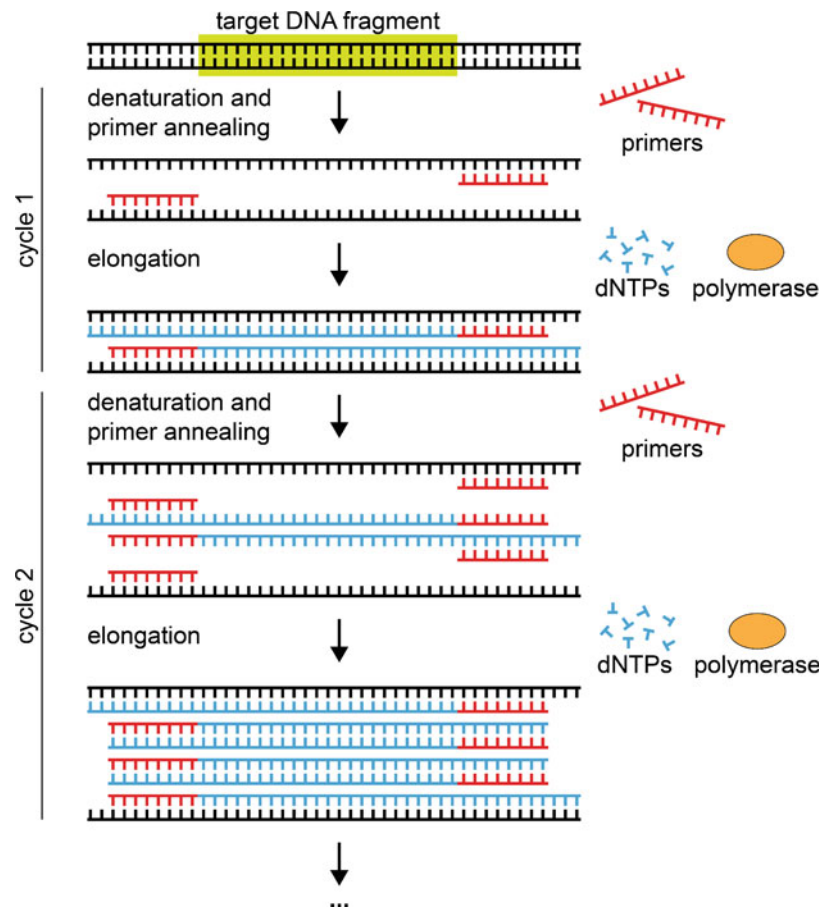


Fig. 1 Schematic presentation of the polymerase chain reaction. Double-stranded DNA is denatured with high temperature. Primers bind to matching sections of the DNA. Polymerase assembles a complementary DNA strand using dNTP building blocks. In each cycle the number of target DNA molecules is doubled

Electron Spin Resonance Dating of Fossil Tooth Enamel

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Synonyms

[Electron paramagnetic resonance \(EPR\) dating of fossil tooth enamel](#)

Definitions

Electron spin resonance (ESR) dating: a chronometric dating method based on the evaluation of the exposure of some materials to natural radioactivity, which is quantified in terms of absorbed radiation dose and corresponds to the energy deposited in the matter by ionizing radiations.

D_E : equivalent dose. The total absorbed radiation dose as measured in the laboratory.

ka: 1,000 years.

Ma: 1,000,000 years.

Introduction

The first ESR dating applications to fossil bones were published in the early 1980s (e.g., Ikeya and Miki [1980](#)). Given the potential of this kind of material, studies were quickly reoriented toward fossil tooth enamel, which has more suitable characteristics for dating (Grün and Schwarcz [1987](#)). Then, the method progressively gained in accuracy over the following decades, especially via a better understanding of the ESR signal of fossil enamel and its behavior with the absorbed dose. A major advance in ESR dating of enamel resulted from the introduction of a method combining ESR and U-series data in order to model the uranium (U) uptake into dental tissues, thus constraining the uncertainty of the resulting dose rate (Grün et al. [1988](#)). This definitely helped to convert the method into a valuable tool to date fossil remains beyond the ^{14}C time range.

Tooth Enamel: A Natural Dosimeter

From a mineralogical point of view, enamel is mainly made of carbonated hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (90 %, vs. ~70 % for dentine and bone), water (~3 %), and organic matter (<1 %) (Elliott [2002](#)). Enamel is denser and more compact than dentine or bone, with larger hydroxyapatite crystals, making it less sensitive to diagenetic changes in terms of microstructure, chemical composition and dissolution/recrystallization processes (e.g., Dauphin and Williams [2004](#); Kohn et al. [1999](#)).

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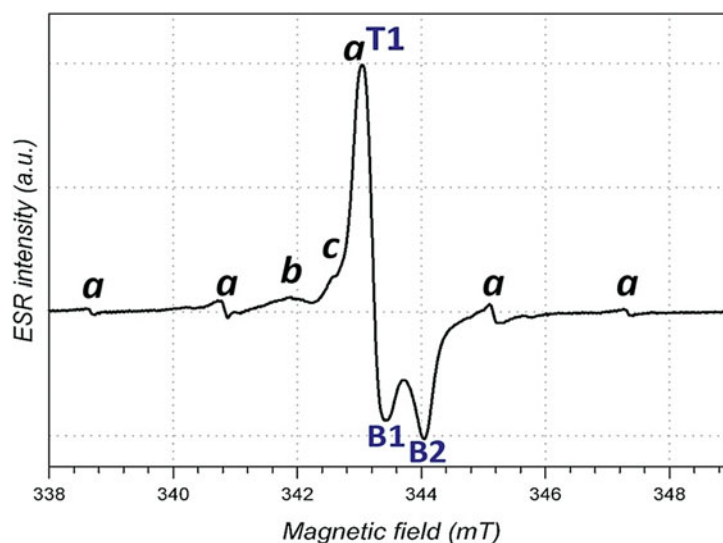


Fig. 1 ESR spectrum of fossil tooth enamel. In addition to the main radiation-induced ESR signal generated by CO_2^- radicals, there are several minor contributions from other species (see Grün 2000b and references therein): (i) there is a septet centered on the main CO_2^- signal at $g = 2.0032$ (labeled “a”; only five lines are visible on that magnetic field range) formed by a free dimethyl radical; (ii) another isotropic line (marked “b”) at $g = 2.0115$ might be attributed to CO_3^- ; and (iii) the isotropic line at $g = 2.0056$ (marked “c”) is usually attributed to a free radical, probably SO_2^- . In ESR dating, ESR intensities are usually extracted by peak-to-peak measurements between T1 and B2.

The dosimetric properties of tooth enamel have been known for more than 40 years (e.g., Brady et al. 1968), and ESR is capable of measuring absorbed dose from only a few tens of mGy to several thousands of Gy (e.g., Fattibene and Callens 2010; Duval et al. 2009). Enamel is now internationally recognized as a valuable natural ESR dosimeter, especially used in the field of retrospective dosimetry for persons accidentally exposed to ionizing radiations (e.g., IAEA 2002 and references therein).

ESR Signal of Tooth Enamel

The ESR signal of tooth enamel is an asymmetric composite signal defined by three peaks at $g \sim 2.0032$ (T1), $g \sim 2.0006$ (B1), and $g \sim 1.9971$ (B2) (Fig. 1). Although many contributors to this signal have been identified (mainly carbonate-derived radicals and some oxygen radicals: Callens et al. 1998; Fattibene and Callens 2010), the major contribution is related to CO_2^- radicals.

Up to seven types of CO_2^- radicals have been identified as contributing to the main radiation-induced ESR signal (Brik et al. 2000), but the system is nevertheless usually simplified by considering three main types of CO_2^- (Fattibene and Callens 2010; Joannes-Boyau and Grün 2011): one isotropic at $g = 2.0006$ and two anisotropic CO_2^- radicals, an axial one ($g_{\perp} \sim 2.003$; $g_{\parallel} \sim 1.997$) and an orthorhombic one ($g_x \sim 2.003$; $g_y \sim 1.997$ and $g_z \sim 2.001$). These CO_2^- radicals are usually divided in two categories: the non-oriented radicals, which exhibit a powder spectrum, and the oriented CO_2^- radicals, whose ESR signal may significantly change according to the angular position of the enamel fragment in the ESR cavity. Both groups have different characteristics in terms of thermal stability or microwave saturation. Furthermore, their relative proportions in the ESR signal may not be the same in the natural and irradiated spectrum. Irradiation or heating processes might induce some transformation from one category to another,

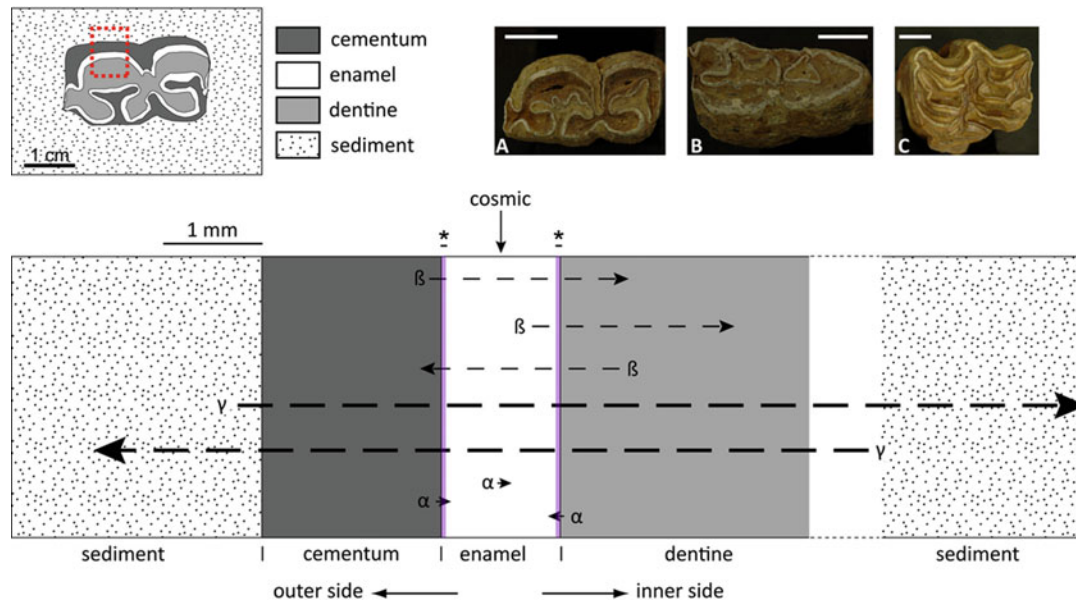


Fig. 2 Tooth geometry for dose rate calculations (Modified from Rink 1997). Shown here is the sediment-cementum-enamel-dentine geometry. (*) is the removed enamel thicknesses (a few tens of μm) from both sides of the enamel layer. *Top right*: examples of occlusal views of horse fossil teeth (**a**, **b**, and **c**) from various Spanish archaeological sites (scale = 1 cm)

which would generate some uncertainties in the evaluation of D_E (Joannes-Boyau and Grün 2011; Brik et al. 2000).

Age and Dose Rate Equations

The basic ESR age equation for tooth dating may be expressed as follows:

where D_E is the equivalent dose, i.e., the total dose (Gy) absorbed by the enamel during the time elapsed between the death of the animal ($t = 0$) and the sampling ($t = T$), and $D(t)$ is the mean dose rate (in Gy/ka or $\mu\text{Gy/a}$).

Basically, the total dose accumulated in the enamel over time is the result of a combination of various contributions coming from radioactivity in the tooth itself and the surrounding environment. The specificity of tooth dating relies on the complex system that has to be considered. Indeed, a tooth is usually made by several tissues of varied thickness and composition. Therefore, accurate age calculation must rely on careful consideration of the geometry of the enamel layer and its surrounding environment (Fig. 2).

Except for the cosmic dose, each component of the dose rate is directly derived from the contributions of the α -particles, β -particles and γ -rays emitted by the radioactive elements located within the sample and its surrounding environment (mainly U and Th decay products as well as ^{40}K). Because each kind of ionizing radiation has a specific penetration range in matter ($\sim 20\text{--}40\ \mu\text{m}$ for α -particles, $\sim 2\ \text{mm}$ for β -particles, and $\sim 30\ \text{cm}$ for γ -rays), some of their respective contribution has to be attenuated or even removed depending on the size of the sample dated.

For dental tissues, only the U decay products contribute significantly to the enamel dose, because tissues are usually assumed to be free of Th decay products as well as ^{40}K (e.g., Grün and

McDermott 1994). Given the typical thickness of the enamel (a few mm), it is usually assumed that self-absorption of internal γ -rays is negligible. Thus, the internal dose rate from the enamel is only made by α - and β -components, which are corrected by an alpha efficiency factor and a self-absorption factor, respectively. For the other tissues, we need to consider only an attenuated beta component, since the external α -particle contribution is removed by abrading both sides of the enamel layer over a few tens of μm . The magnitude of the beta component depends on the initial and removed thicknesses of the enamel layer as well as water content in the tissues. Finally, the sediment typically provides only a γ -ray contribution to dose rate (unless the enamel is in direct contact with sediment), corrected by water attenuation, and derived from the measured elemental concentrations of U, Th, and K. Consequently, in case of a geometry sediment-cementum-enamel-dentine (Fig. 2), the dose rate equation may be expressed as follows:

where $C_{\text{U, Th, K}}$ is the concentration in U, Th, and K measured in each dental tissue and sediment; $W_{\alpha, \beta, \gamma}$ is the water attenuation for α -particles, β -particles, and γ -rays; $F_{\text{U, Th, K; } \alpha, \beta, \gamma}$ is the dose rate conversion factor depending on the kind of ionizing radiation and the emitter; k is the alpha efficiency; $S_{\text{U}\beta}$ is the internal beta self-absorption; and $A_{\beta 1,2}$ is the external beta attenuation for U-series elements. Equation (2) is valid when equilibrium is assumed within the U-series or Th-series decay products in the dental tissues and sediment. However, if disequilibrium is observed, more elements in each decay series have to be considered in the equation. Specific issues with disequilibrium in dental tissues and sediment may be found in Grün (1989) and Olley et al. (1996), respectively.

In case of enamel in direct contact with the sediment, Eq. (2) has to be modified by considering an external beta contribution from the sediment, instead of a tissue.

U-Uptake Modeling

Dental tissues behave as open systems for U-series elements. It is therefore crucial not only to measure the U-content but also to know its past evolution. To address this point, several parametric U-uptake models were proposed. The early uptake (EU) model assumes that U is incorporated shortly after burial (Bischoff and Rosenbauer 1981), i.e., an approximation of a closed system. The linear U-uptake (LU) model describes uptake with a constant rate since the time of burial (Ikeya 1982). The recent uptake (RU) model considers that all measured U-concentration in the sample was taken up in very recent times (Blackwell et al. 1992). These parametric models allow some easy age calculations, but are based on unrealistic assumptions (i.e., the closed system assumption for the EU uptake). Additionally, the models oversimplify the complexity of U-uptake into the different tissues in some teeth (e.g., Grün 2009a). These models cause large uncertainties when uranium concentrations in the dental tissues are high, and the calculated age value may be then very sensitive to the U-uptake assumption (e.g., Grün and McDermott 1994; Duval et al. 2012).

To address the problem of the unknown U-uptake, Grün et al. (1988) suggested to combine ESR and U-series analyses and introduced a parameter p to describe the kinetics of the U-uptake in the dental tissue (US model). In comparison with the conventional models, the combined US-ESR method has the advantage that U-uptake history is not a priori assumed, but mathematically assessed according to the ESR and present-day U-series (U-concentration, $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$) data measured in each tissue. As a consequence, only one combined US-ESR age fits the available dataset (Grün et al. 1988). Moreover, the US-ESR approach considers the possibility of different uptake histories among the various dental tissues of a unique tooth, by calculating

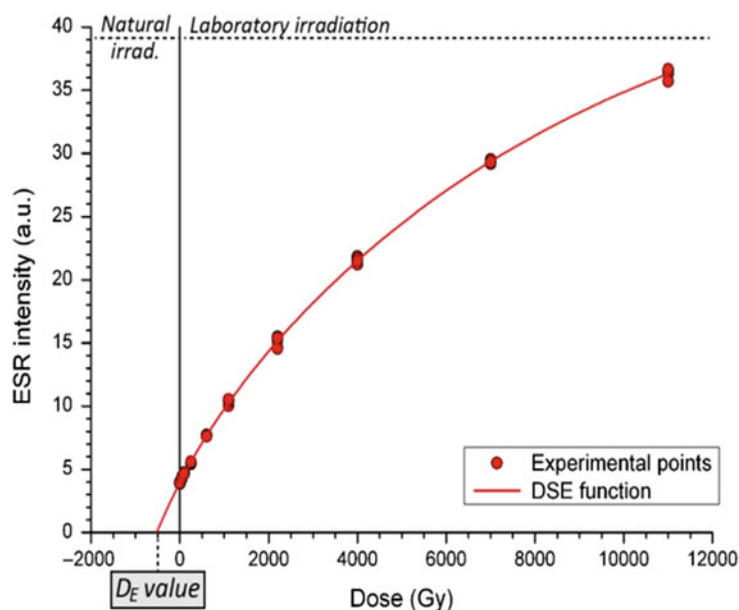


Fig. 3 Example of ESR dose–response curve. A double saturating exponential (*DSE*) function is fitted through the experimental points, and D_E is obtained by extrapolation of the function to $Y = 0$

a specific p -parameter for each tissue. This approach also helps to overcome some limitations of the U-series dating method in some specific situations, beyond the time range of the U-series dating method (Grün et al. 2010) or in case of very recent U-uptake (e.g., Falguères et al. 2006).

However, the combined US-ESR approach has also several limitations. First, U-leaching from dental tissue cannot be modeled (Grün et al. 1988). By definition, the U-uptake history is mainly modeled from the U-series data measured in dental tissues. Consequently, the reliability of the calculated age is highly dependent on the accuracy of these U-series data. However, the latter may be influenced by many factors, such as the spatial homogeneity and preservation of the sample, or recent U-mobilization that may overprint past U-uptake history (Duval et al. 2011). Other models based on the combination of U-series and ESR data have been also developed, in particular to specifically address the issue raised by the occurrence of U-leaching in dental tissue (e.g., Shao et al. 2012) or the spatial variation of the U-series data (Pike et al. 2001), but their potential and limitations are not clearly defined yet. Finally, another variation of the US model was also proposed by Grün (2000a), the closed system (CS)-US model. This is based on a very specific assumption, i.e., the measured uranium content was incorporated into the tissues at the time corresponding to the apparent U-series age, providing thus a maximum possible age for the sample.

Standard Analytical Procedure: A Brief Overview

An ESR age estimate is the result of a long and complex analytical process, made by several steps associating fieldwork and laboratory procedures, which may be resumed as follows:

Sampling. Fossil teeth are collected directly from the site or chosen from collections. In situ measurements of the natural radioactivity should be performed at the exact place, or at least the closest possible, where the sample was collected.

Sample preparation. In the laboratory, the tooth is prepared by separating mechanically each dental tissue. The enamel is then cleaned on both sides to remove external α -particles contribution

and powdered, in order to avoid angular dependence of the ESR signal within the ESR resonator and to improve sample homogeneity.

D_E reconstruction by ESR spectrometry. The enamel powder is usually divided in one or several subsample aliquots that are irradiated at various increasing dose steps (additive dose method). Each aliquot is then measured at room temperature by X-band ESR spectrometry in order to study the behavior of the ESR signal with the increasing dose values. The ESR intensity is extracted from each spectrum, usually by peak-to-peak measurements between T1 and B2 (Fig. 1). A mathematical function, usually a single saturating exponential or a double saturating exponential function (Duval et al. 2009), is fitted through the experimental data points and its extrapolation to the abscissa axis ($Y = 0$) provides the D_E value, corresponding the total dose absorbed by the tooth enamel since the death of the animal (Fig. 3).

Evaluation of dose rate. If the gamma dose rate has to be assessed in situ, the external beta dose rate contribution coming from the sediment should be assessed in the laboratory, from the sediment sample that was collected around the tooth. Usually, the dose rate is derived from the activities or concentrations of the radioactive elements present in the sample and its surroundings. These concentration data are converted into dose values using known factors (Guérin et al. 2011) and corrected according to several parameters, such as the water content (e.g., Grün 1994), the geometry of the sample, its thickness and density for β -attenuations (Brennan et al. 2000), and the alpha efficiency (Grün and Katzenberger-Apel 1994). In case of the combined US-ESR approach, U-series data from each dental tissue (U-concentration, $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$) is required in order to model the uranium uptake. Finally, the cosmic dose rate contribution is usually assessed via tables and is corrected according to various factors like the ground density, depth of the sample, altitude, and latitude (Prescott and Hutton 1994).

ESR age estimate. Basically, two main non-commercial programs are most widely used for age calculation on teeth: these are the ROSY software which enables age calculation based on the parametric U-uptake models (Brennan et al. 1999) and the DATA program, providing combined US-ESR age estimates (Grün 2009b). ESR ages are usually quoted $\pm$ one standard deviation. Relative age uncertainties are rarely $<10\%$ (Rink 1997) and are more likely between 10 % and 20 %.

Time Range Applicability

It is usually considered that the optimum time range application for ESR dating of tooth enamel lies between ~ 50 and ~ 600 ka. Nevertheless, under some specific conditions, the time range limits may be potentially pushed from <1 ka to $\sim 2\text{--}3$ Ma.

For modern ESR samples, the lower dating range is in general mainly driven by (i) the radiation sensitivity of the material and (ii) the sensitivity of the tools employed for dose reconstruction, including the ESR spectrometer. Recent developments in ESR dosimetry of enamel lead to define a detection limit of several tens of mGy (Fattibene and Callens 2010). The detection of background dose values with ESR spectrometry (e.g., Toyoda et al. 2011) suggests the possibility of dating almost present-day (i.e., last millennium) materials, as soon as radionuclide concentrations in the sample and its surrounding environment can be accurately assessed. However, a rapid overview of the published works indicates that ESR dating is rarely applied to fossil teeth younger than ~ 20 ka.

The upper limit of the datable age range is mainly constrained by two parameters: (i) the saturation of the ESR signal with the absorbed dose and (ii) the thermal stability of the paramagnetic centers. Depending on the number of traps available in the crystal lattice, the nature of the

analyzed paramagnetic center and the intensity of the dose rate, the intensity of the ESR signal may saturate rapidly or more slowly when the material is absorbing ionizing radiations. In the case of teeth, the saturation level in enamel is very high and absorbed dose values up to several thousands of Gy have been detected (e.g., Duval et al. 2009). The second parameter is the thermal stability of the paramagnetic centers, which describes the mean life of a trapped electron at the defect site. Schwarcz (1985) assessed the lifetime of the ESR signal of tooth enamel to ~1 Ga at 25 °C, suggesting then a possible application over a few Ma. As a rule of thumb, the ESR signal must have a mean life of at least one order of magnitude higher than the age of the sample dated (Grün 2007) in order to avoid systematic uncertainties due to decay of the signal during burial. However, when dealing with old samples (>800 ka), the main complication lies in the U-uptake modeling for the dose rate reconstruction. Indeed, U-leaching may be frequently observed for such time range, making the application of the combined US-ESR approach extremely difficult (e.g., Duval et al. 2012). Only two situations are possible in which ESR dating could potentially be accurate to ages up to ~2–3 Ma: (i) no apparent U-leaching is detected in dental tissues, which may sometimes occur for Early Pleistocene sites (e.g., Duval et al. 2012), or (ii) the tooth samples show very low U-concentration in dental tissues (e.g., Schwarcz et al. 1994), decreasing the relative contribution of dental tissues in the total dose rate calculation in comparison with sediment.

Main Strengths and Weaknesses of the ESR Dating Method Applied to Fossil Teeth

ESR dosimetry of tooth enamel is now an international reference method (Fattibene and Callens 2010), demonstrating the great potential of this material for dose reconstruction. In addition, ESR is one of the very few dating methods that may be applied to fossil remains and can provide a direct measurement of age of hominid or animal occupation in any sedimentary context. ESR dating is also one of the very few alternatives for dating fossils, including hominid remains, beyond the ¹⁴C and U-series dating time range (Grün et al. 2010).

In contrast, the complexity and the length of the analytical process are likely the main limitations of this dating method. Many parameters (>15) have to be considered and assessed for the age calculation, with a direct consequence on the age precision (final age errors are usually > 10 %). In addition, at least several months are usually required to fully process a sample, and the analytical procedure involves an array of equipment that must be carefully and accurately calibrated (e.g., U-series analyses facilities, ESR spectrometer, gamma irradiation source, high-resolution gamma spectrometer, portable gamma spectrometer). Finally, another limitation lies in the sampling itself. In the case of historic excavations, it may be difficult to precisely locate (geographically and stratigraphically) the sample's provenance, which induce many uncertainties on the external dose rate associated to sediment and thus on the final age estimate.

Some Examples of Recent Developments in the Field

ESR Measurement of Enamel Fragments

Working with enamel fragments significantly reduces the destructive aspect of the method. However, this technique implies a complex analytical procedure (e.g., Joannes-Boyau and Grün 2011). Nevertheless, ESR analyses of enamel fragments, unlike powder, may provide useful information about the composition of the ESR signal: each component contributing to the

radiation-induced ESR signal may be potentially isolated and studied separately, which may be of special interest for reducing potential source of error in the D_E assessment (Joannes-Boyau and Grün 2011).

High-Resolution Mapping of Radioelement Distribution in Dental Tissues

The combination of a laser ablation system with an ICP-MS (LA-ICP-MS) recently opened huge perspectives for the U-series analyses of dental tissues (e.g., Eggins et al. 2003), yielding high-resolution U-series data in a short acquisition time and with minor sample preparation. For example, maps of spatial distribution of U-series elements in dental tissues may be obtained (e.g., Duval et al. 2011). This is of special interest for studying U-mobility into dental tissues and may be particularly useful to identify domains in the teeth that are suitable for ESR dating.

Direct Dating of Hominid Remains

The recent development of ESR measurements on enamel fragments combined with LA-ICP-MS U-series analysis now permits analysis of human teeth without causing any visible damage (e.g., Grün et al 2006). Such an approach offers new perspectives for the ESR method, by giving access to direct dating of inestimable hominid remains that are beyond the ^{14}C time range.

ESR Dating of Early Pleistocene Fossil Teeth

“Old” samples result in many challenges that are not encountered in younger samples and which make the application of the combined US-ESR approach especially complex (see Duval et al. 2012 for further details). Nevertheless, recent methodological developments showed that ESR may be a useful tool to constrain the chronology of the earliest hominid occupations in Eurasia and Africa during Early Pleistocene times (e.g., Duval et al. 2012).

Summary

ESR dating is one of the very few dating methods that may be applied to fossil remains, resulting in a direct measurement of the age of hominid or animal occupations in any sedimentary context. The challenge in applying ESR dating to fossil teeth lies in the requirement to model U-uptake kinetics into dental tissues, which are known to behave as open systems for U-series elements. So far, the combined (or coupled) U-series/ESR dating approach provides the most reliable ESR age estimates. Under some specific conditions, this application may potentially cover the whole Quaternary time range.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Bones, \(U-Series\)](#)
- ▶ [Electron Spin Resonance Spectrometer](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating - General Principles](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating of Coral](#)
- ▶ [Geochronology](#)
- ▶ [Hominid Evolution Timescale](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)

- [Neutron Activation Analysis](#)
- [Radiation and Radioactivity](#)
- [Radiation Dose Rate](#)
- [Radiation Defect](#)
- [Sediment \(ESR\)](#)
- [Teeth \(ESR/U-Series\)](#)
- [Thermal Ionization Mass Spectrometer \(TIMS\)](#)

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Luminescence, Desert Dunes

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Synonyms

Dune chronostratigraphy; OSL dating

Definition

Luminescence dating. Geochronological method relying on the dosimetric properties of common minerals to accumulate a trapped charge proportional to burial age and the dose rate.

Desert dunes. Discrete aeolian landforms, typically dominated by sand, found in dryland regions of the world.

Introduction

In many respects, desert dunes are the ideal medium for the application of luminescence dating. They are typically dominated by sand-sized quartz, occur in an environmental setting typified by intense sunlight and relatively rapid aeolian sedimentation (leading to well-defined “bleaching” events), and are usually characterized by a lack of other dateable material. Crucially, their dynamism overlaps very closely with the typical range of timescales to which luminescence dating is applicable (i.e., $10 - 5 \times 10^5$ years). It is, thus, unsurprising that it was desert dunes that saw the first geoscience application of luminescence dating, with Singhvi et al.’s (1982) landmark geochronological study of the Indian Thar desert. The earliest studies used heat as the stimulation source (thermoluminescence, or TL), and indeed TL continued to be applied to dune sequences routinely for the next 20 years or so, but Huntley et al.’s (1985) use of light (Optically Stimulated Luminescence, or OSL) has become by far the most commonly used method today. It was not, however, merely the ability to date dunes directly for the first time that drove a rapid expansion in interest in luminescence dating of desert dunes; the research agenda was driven primarily because it had long been recognized that desert dunes are among the most dynamic and environmentally sensitive of earth’s terrestrial systems.

The Growth of Luminescence Dating of Desert Dunes

Despite Pye and Tsoar’s (1990) cautious assertion that “many difficulties remain to be resolved before luminescence dating of sand can be regarded as entirely reliable,” a key feature of today’s research was established early on; it was not generally the active dunes of the world’s hyperarid regions that attracted the most attention. It was the fully or partially stabilized dunes of the desert

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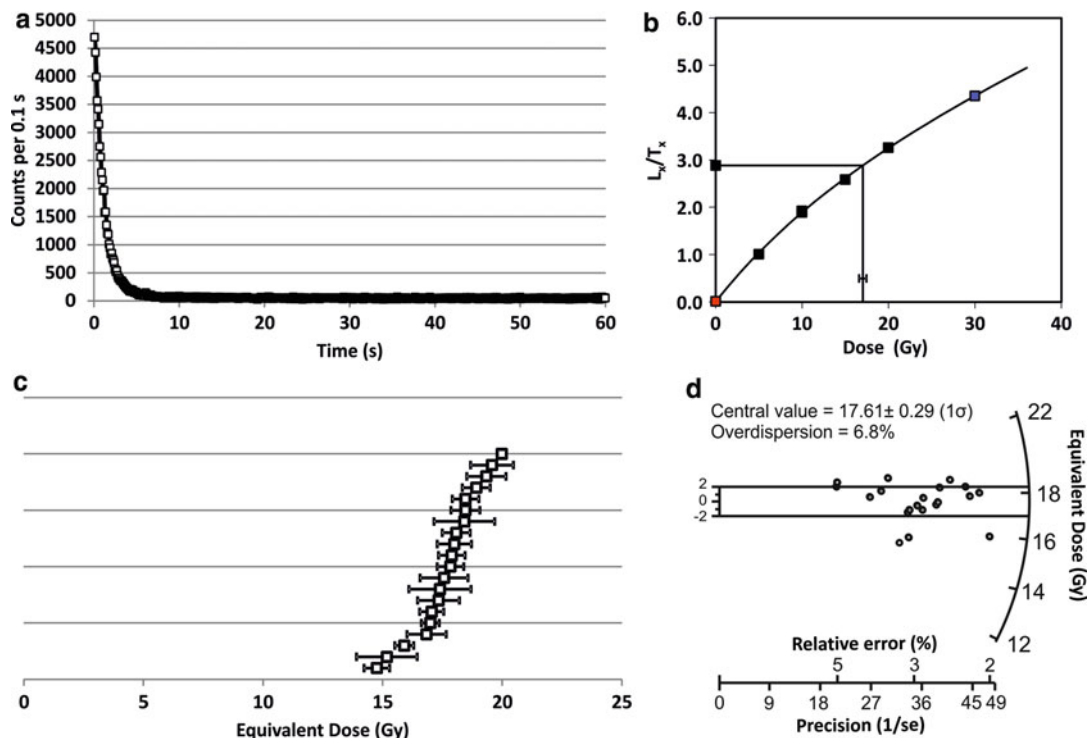


Fig. 1 Many studies have found desert dunes present an ideal medium for luminescence dating, with samples demonstrating: (a) bright, fast-component-dominated quartz OSL signals; (b) well-defined growth curves with low recuperation and good recycling characteristics; (c) and (d) good repeatability of equivalent dose measurements between aliquots, shown here as both as ranked and radial plots

margins. The dunes of Australia (e.g., Gardner et al. 1987), Southern Africa (e.g., Buch et al. 1992), and the Western USA (e.g., Stokes and Gaylord 1993) attracted particular attention. These studies investigated a wide range of dune morphologies. Many studies focused on individual sites or localized areas, but some, notably Nanson et al. (1992) and Stokes et al. (1997), were more ambitious in scope, aiming to provide regional-scale syntheses of late Quaternary aridity. In general, desert dunes proved highly favorable for the method, typically offering well-defined growth of the OSL signal and excellent repeatability (best defined by overdispersion sensu (Galbraith et al. 1999)). Figure 1 demonstrates a typical shine-down curve, growth curve, and dose distribution for a favorable desert dune sample. Thus, the majority of studies have focused less on the technical suitability of dune sands for luminescence dating and more on the interpretation of the results of the dating work.

Some studies (e.g., Lomax et al. 2007), however, have encountered poor repeatability of individual aliquots (i.e., high overdispersion) from dune sands. Such effects are usually attributed to heterogeneous dose environments, inadequate bleaching at time of deposition, or postdepositional mixing of sediment. The latter is often considered the most significant problem in massively bedded desert dunes and has been investigated in detail (Bateman et al. 2007). The low moisture levels and typically homogeneous sediment are also usually assumed to lead to straightforward estimation of the dose rates, but as in other environmental settings dated with luminescence, dosimetric issues have perhaps sometimes been overlooked. In dunes which have periodically accumulated over long periods of time, the cosmic contribution to dose rate may be better estimated by an iterative procedure to model the varying overburden (Munyikwa 2000). Commonly assumed moisture contents for dunes may also have frequently been overestimated (Telfer and Hesse 2013).

Desert dune sands have also been used in methodological development of luminescence dating, although perhaps less frequently than might be expected, perhaps due to the difficulty of corroborating ages derived from new techniques with alternative dating methods. Nonetheless, Li and Li (2011) have applied post-IR IRSL (Infra-Red Stimulated Luminescence) to Chinese dune sands, with a view to extending the applicable age range of the method, and Fujioka et al. (2009) paired OSL and cosmogenic dating techniques to date the inception of an Australian dune field. Field methodologies have perhaps developed more rapidly in the study of desert dunes, with geophysical survey and augering methods used to achieve full-depth survey and sampling of dunes up to around 20 m depth. In a very few instances (e.g., Preusser et al. 2002), heavy duty coring equipment has been used to extract dateable sand cores in excess of 150 m length, but challenges remain with the recovery rate of such loose sediment.

Applications of Luminescence Dating of Desert Dunes

Although the methodological challenges of luminescence dating of desert dunes are less than some other environments (e.g., fluvial or glacial), the interpretation of ages obtained from dunes remains highly complex. The majority of studies of desert dunes around the turn of the millennium remained focused on paleoenvironmental studies, often with a view to paleoclimatic interpretation of the data; a significant minority of research, however, used the ability to provide chronometric control for dune development to improve understanding of geomorphology. It must be borne in mind that most dune systems will have involved repeated cycles of deposition and erosion, and an OSL age refers only to the most recent of these burial events, with important possible implications for the contextual interpretation of the age.

A wide range of dune types has been studied, with different dune types attracting different types of study on account of their differing geomorphological characteristics. For instance, the transition from active barchan dunes to stabilized parabolic dunes on the Canadian prairies over a period of ~200 years has been described by Wolfe and Hugenholtz (2009). Linear dunes are typically considered much more long-lived landforms, as their mode of formation does not lead to such frequent complete reworking of the dune body, and hence these are often seen as offering the greatest potential for long-term records of past aeolian environments. Star dunes, which include the largest dunes on earth, have proven challenging for dating studies, with full-depth sampling of large star dunes not currently achieved, but they have occasionally formed part of investigations into complex dune patterns (Beveridge et al. 2006).

Paleoenvironmental Applications

The prevailing paradigm of the 1990s was broadly that increased frequency of observed ages within a currently stabilized dune equated to past periods of aridity, although there were already conceptual models which suggested that dryland landscape response to external forcing stimuli may be more complex than this (Kocurek 1998). Some long-standing hypotheses were challenged, such as the assumption that the widespread arc of currently stabilized dunes in Southern Africa resulted from drier conditions during the Last Glacial Maximum (LGM) (O'Connor and Thomas 1999). Dunes offer a rare opportunity to establish paleowind directions, which has been exploited at both continental (e.g., Nanson et al. 1995) and regional scale (e.g., Holmes et al. 2008). Luminescence dating also allowed the direct dating of sites of high archaeological significance, such as the human remains from the lunette dune at Lake Mungo, Australia.

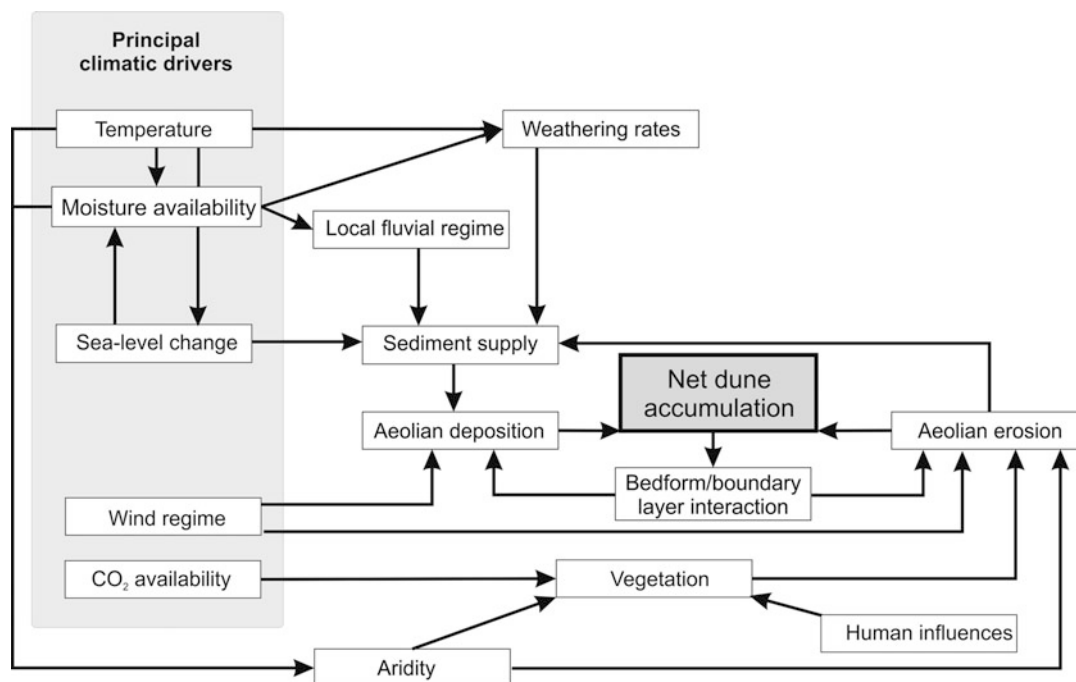


Fig. 2 Conceptual model of the drivers of net dune accumulation under changing climatic regimes, demonstrating the complexity of the linkage between external drivers and landform response. The presence of bedform/boundary layer interaction as a result of changes in aeolian accumulation is perhaps the most significant aspect introducing non-linearities into the system. This schematic is not intended to be exhaustive, and numerous other linkages and feedback could be proposed

More recently, however, a number of studies have begun to challenge the assumption that frequency of observed luminescence-derived dune ages is a direct proxy for past aridity. There are a number of reasons for this, and perhaps the most important is the spatial and temporal variability evident in the preservation of dune sands. As most dunes rework themselves during periods of reactivation, the sedimentary record from dunes is typically discontinuous. Some studies showed that adjacent dunes did not respond identically to what must have been identical climatic forcing (Telfer and Thomas 2007). Stone and Thomas (2008) sampled a dune at 0.5 m vertical intervals – a better resolution than had previously been attempted – and noted that if these data were subsampled to 1 m resolution (i.e., jack-knifing), there was worrying disparity between the conclusions drawn from some of the older ages. Such studies implied that the stochastics of net preservation in dune systems were complex and led Telfer et al. (2010) to investigate such interpretations via modeling, which suggested that current sample sizes were in most cases inadequate to interpret anything other than gross trends in the net accumulation rate in dunes.

Concurrent with increased realization of the implications of spatial variability in the preservation of dune records came increased questioning as to what the record of OSL-derived chronostratigraphies actually meant from a paleoenvironmental, or even paleoclimatic, perspective. Traditionally, an increase in observed frequency of dated samples was interpreted as increased aridity (e.g., Stokes et al. 1997). More recent work has identified a very wide range of possible drivers of net dune accumulation rates, and the complexity of the factors affecting dune accumulation is shown in Fig. 2 and must be considered site specific. The interpretations of Roskin et al. (2011) are a good example of current best practice, drawing in a wide range of additional data before drawing inferences on the driving factors in the region under investigation.

Geomorphological Applications

There have been fewer chronological studies of dunes with geomorphology as the primary aim, but those that have addressed processes and rates of landform formation have often been very successful. Luminescence-constrained chronologies offer a longer-term perspective than observational studies can allow, and although some dunes do currently move on timescales that can be usefully monitored in the field, or using remotely sensed data, it is also clear that many dunes have formed on timescales greater than 10^3 years.

In some instances, luminescence dates have been used to constrain the sequence of events in complex aeolian environments, thus helping in the understanding of complex interactions and feedbacks operating between the bedform and the moving atmospheric boundary layer (Lancaster et al. 2002). Luminescence dating has also been used at the landform scale to help elucidate long-term landform development, particularly in combination with ground-penetrating radar (GPR) to reveal internal stratigraphy of dunes (Bristow et al. 2005; Bristow et al. 2007). Telfer (2011) demonstrated that with sufficient sampling resolution, chronostratigraphies alone could inform long-term landform evolution studies, by demonstrating the complex extension of a Kalahari linear dune. Attempts have also been made to use the luminescence characteristics of dune sands to determine whether the dunes were formed in subaerial or subaqueous environments (Burrough et al. 2012).

Summary and Conclusions

Desert dunes are typically some of the least challenging environments in terms of getting successful luminescence dates. The challenge comes with the interpretation of these dates. It is not possible to take a limited number of samples in a nonsystematic manner from a stabilized dune field and extract a regional climatic signal of aridity. There is an urgent need for improved understanding of the long-term process geomorphology of dunes, and currently, the best way of using dunes as a geomorphological proxy of past environments is to consider them alongside other paleoenvironmental archives and to recognize the complexity of the climate change-landscape response relationship in dunes. That said, luminescence dating of dunes still offers an essential tool for understanding the nature and rates of aeolian processes at scales beyond those which can be observed directly. This will prove vital in the future for improved understanding of dryland landscape response to changing external stimuli, a pressing issue in the light of twenty-first-century climatic change.

Cross-References

- [Luminescence Dating](#)
- [Luminescence Dating of Archaeological Sediments](#)
- [Luminescence Dating, Dose Rate](#)
- [Luminescence Dating, History](#)
- [Luminescence Dating, Instrumentation](#)
- [Luminescence Dating, Single Grain Dose Distribution](#)
- [Luminescence Dating, Uncertainties and Age Range](#)

- [Luminescence, Loess](#)
- [Luminescence, Soils](#)
- [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)

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Amino Acid Racemization Dating

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Synonyms

[AAR, Protein diagenesis geochronology](#)

Definition

A method for estimating the relative age since death by assessing the extent of postmortem conversion of biological chiral forms of amino acids (L-enantiomers) to their nonbiological counterparts (D-enantiomers).

Introduction

Amino acid racemization (AAR) dating is a geochronological technique with a very long history. Over the past 60 years, many researchers and laboratories around the world have been involved with the development of the method and its application to diverse environments. Its time depth and applicability to a wide range of substrates are the main strengths of this method. Its main weakness is the fact that it is a molecular- rather than an atomic-scale reaction (cf. radionuclide decay), and as a consequence the rate is sensitive to temperature. Useful review articles for understanding the principles of AAR dating are those of Miller and Brigham-Grette (1989), Mitterer (1993), Rutter and Blackwell (1995), Johnson and Miller (1997), and Wehmiller and Miller (2000). In addition, two classic volumes on amino acid racemization were produced: *Biogeochemistry of Amino Acids* (1980), edited by Hare, Hoering, and King, and *Perspectives in Amino Acid and Protein Geochemistry* (2000), edited by Goodfriend and colleagues. Following a session on AAR dating that took place at the INQUA 2011 conference (Bern, Switzerland), a special issue of the journal *Quaternary Geochronology* (vol. 16, pages 1–198, April 2013, edited by Penkman and Kaufman) was published in 2013. This summarizes the current state of the art in AAR research. We refer the interested reader to these publications for gaining a more in-depth understanding of the vast field of protein diagenesis and its applications to geochronology.

Here we provide a basic toolkit for understanding the principles of AAR, beginning with the chemical mechanisms of protein diagenesis, summarizing briefly the history of the development of the technique, and then focusing in more detail on one of the methodologies of AAR dating that has been developed in more recent years: the intracrystalline protein diagenesis (IcPD) approach. While the method does not supersede more traditional approaches, it is an important step towards the integration of AAR and biomineralization studies. The two are deeply intertwined, as biomineral growth is controlled by proteins which are then trapped in the mineral framework and undergo postmortem degradation. Therefore, understanding the complexities of protein diagenesis should be

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viewed in conjunction with an understanding of biomineral formation which, after death, will represent the protein's burial environment.

We refer to the following entries in this *encyclopedia* for additional information:

- ► [Amino acid Racemization, Arctic Environment](#)
- ► [Amino acid Racemization, Biostratigraphy](#)
- ► [Amino acid Racemization, Coastal Sediments](#)
- ► [Amino acid Racemization, Eggshell](#)
- ► [Amino acid Racemization, Eolianites](#)
- ► [Amino acid Racemization, Fluvial and Lacustrine Sediments](#)
- ► [Amino acid Racemization, Loess and Glacial Sediments](#)
- ► [Amino acid Racemization, Marine Sediments](#)

What Is an Amino Acid?

Amino acids, the building blocks of proteins, share a common chemical character, each containing a hydrogen atom (H), an amino group (NH_2), a carboxyl group (COOH), and an (R) group, or side-chain, bound to a central carbon atom (C). Amino acids have both amine and carboxylic acid functional groups and therefore can act both as an acid and as a base. Most proteins are built from sequences of 20 different amino acids; their chemical characteristics are determined by the –R group and their sequence in the protein by the genetic code (Fig. 1).

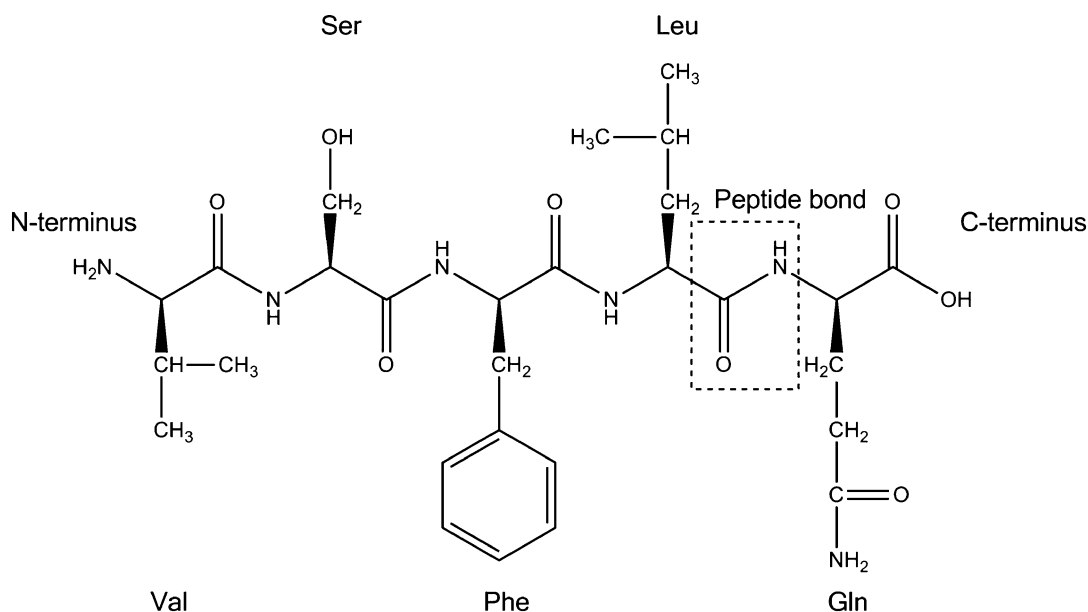


Fig. 1 A short peptide (Val-Ser-Phe-Leu-Gln) to illustrate side chains (–R groups) and the backbone structure formed by the condensation between the amino and carboxyl group of two amino acids (peptide bond). Proteins are typically composed of 50–1,000s amino acid residues

What Is Amino Acid Racemization?

Chirality

Consider your hands; left and right (in Latin, left is *laevo*, and right is *dextro*). Your hands have chiral symmetry: they are mirror images of each other and cannot be superimposed. As with your hands, so with all but the simplest molecules: the configuration of their atoms in space means that they too can exist in more than one form, which may be mirror images but cannot be superimposed. All of the amino acids that occur in proteins, except for glycine, which is the simplest amino acid, have at least one asymmetric carbon atom. They can therefore exist in two nonsuperimposable stereoisomers (enantiomers), termed (from the Latin) L- and D-forms. Some amino acids have two asymmetric carbon atoms and can exist in four different forms, known as diastereomers. Two of these amino acids, isoleucine and threonine, are commonly found in most proteins. L-isoleucine racemizes (or more accurately in the case of two asymmetric carbon atoms, epimerizes) almost exclusively to one form, called D-alloisoleucine. Because diastereomers have different chemical and physical properties, they are the easiest to measure and were therefore the first to be used for geochronology.

Dating

The basis of amino acid racemization (AAR) as a dating technique is the measurement of the relative proportions of the L- and D-chiral forms. In almost all living proteins, amino acids are present in the L-form. The most commonly encountered exceptions are bacterial cell wall biopolymers, collectively termed peptidoglycan. The presence of D-amino acids in peptidoglycan is a potential confounding factor, although it is useful to estimate microbial reworking.

Upon death L-amino acids will slowly and spontaneously convert to D-amino acids, which themselves spontaneously revert back to the L-form. Eventually, a situation of dynamic equilibrium is reached, where there is a 1:1 (so-called racemic) mixture of L- and D-amino acids. A simple mnemonic is that L-forms are found in “living” organisms and D-forms accumulate in “dead” ones. This interconversion reaction is called **racemization**.

Racemization analysis has been conducted on wood (Engel et al. 1977), on textiles (Moini et al. 2011), and in the biosciences on a range of tissues (skin, arteries, cornea) (Ritz-Timme and Collins 2002), but for geochronology **biominerals** are the preferred target. Amino acids have been reported in pyrite and have been isolated from soils and rocks, siliceous sediments, and bioapatites (enamel) (e.g., Kimber et al. 1994; Nardi et al. 1994; Hearty and Kaufman 2000; Murray-Wallace et al. 2001; Harada et al. 2002; Griffin et al. 2009), but most studies focus on **carbonate** biominerals, principally aragonite and calcite: mollusk shells, eggshell, ostracods, foraminifera, brachiopods, and corals (a selection of studies on carbonate biominerals: Bada et al. 1970; Wehmiller and Hare 1971; Wehmiller 1976, 1977, 1980, 1982; Masters and Bada 1978; Andrews et al. 1979; Davies 1983; Hearty et al. 1986; Miller et al. 1983; Müller 1984; Brooks et al. 1990; Goodfriend 1992; Bates 1993; Sejrup and Haugen 1994; Wehmiller et al. 1995; Goodfriend et al. 1996, 1997; Torres et al. 2000; Kaufman 2003; Barbour Wood et al. 2006; Kaufman et al. 2008, 2013; Hendy et al. 2012; Ortiz et al. 2013; Penkman et al. 2007, 2013).

Racemization proceeds at different rates according to (a) the chemical characteristics of the amino acid itself, (b) the position of the amino acid within the protein, and (c) burial temperature and other factors (pH, water availability, presence of cations and anions, microbial degradation). As we will see, factors operating in the burial environment can be *better* controlled if a closed-system fraction of amino acids (“intracrystalline”) is used for dating purposes. If all of these variables are known (or comparable between a set of samples), then the ratio between the D- and L-forms of a specific amino acid (also called D/L value) will reflect the age since death of the organism. This ratio will increase over time from a value of 0 (when the organism is alive, and no D-amino acids are present) to

1 (racemic equilibrium, where a 50–50 % mixture of L- and D-forms is present). Therefore, for a series of samples of increasing age, the D/L value will also increase: this is the basis for building relative chronological frameworks with AAR. These frameworks can then be calibrated, if the D/L value is measured on samples of known age – for example, a series of shells that have been dated by radiocarbon (Kosnik et al. 2008). This allows building calibrated chronological frameworks, which can then be used to date samples independently. However, many studies focus on Quaternary deposits, which lie well beyond the radiocarbon range: in this case, calibration must rely on other independent chronologies, for example, U-series, OSL, strontium isotopic stratigraphy, paleomagnetism, biostratigraphy, and sedimentary evidence (e.g., Wehmiller and Belknap 1982; Hearty et al. 1986; Penkman et al. 2011; Wehmiller et al. 2012). Calibration is especially important because pre-Holocene samples have experienced a number of glacial-interglacial cycles and have therefore been exposed to different burial temperatures, which prevent Holocene-based calibrations to be extended back to the Pleistocene (see also “► [Amino Acid Racemization, Paleoclimate](#)”).

A Brief History of the Technique

The first report of the presence of amino acids preserved in geological samples was in 1954 when Philip Abelson from the Carnegie Institute in Washington DC undertook chromatographic analysis of a number of fossil samples, including fossil fish more than 300 million years of age (from the Devonian Period) (Abelson 1954). Once the group switched to ion exchange chromatography, they noticed the presence of the nonbiological amino acid alloseucine (alle) in some fossil samples and speculated that this was perhaps the result of an age-dependent chemical reaction. Ed Hare from the same institute understood that the epimerization of Ile into alle was a potential tool for geochronology and that as epimerization is a chemical reaction governed by time and temperature, the levels of alle would increase in progressively older samples. This was demonstrated by the experiments of Hare and Mitterer (1969), who measured the rate of racemization of L-isoleucine to D-alloseucine in modern shell fragments heated at high temperatures; they then extrapolated these data to lower temperatures in order to estimate the rate of racemization of L-isoleucine in fossil shells to obtain what they believed to be an approximate age for these fossil shells.

This work blossomed in the 1960s with Ed Hare, Tom Hoering, John Wehmiller, Kenneth King Jr., Richard Mitterer, Sidney Fox, and Kaouru Harada, among others (see the *Mercenaria* Scientific Family Tree that was presented to Ed Hare in occasion of his retirement in 1998) rapidly expanding their range of analyses and substrates. The focus was primarily on understanding the processes and mechanisms of degradation: a range of studies on marine sediments, for example, exploited the stable thermal environment at the bottom of the sea in order to decouple the effects of age and temperature on the processes of racemization and therefore elucidate the kinetics of isoleucine epimerization (Wehmiller and Hare 1971; Bada and Schroeder 1972; Kvenvolden et al. 1973).

Almost in parallel at UC San Diego (SCRIPPS), Jeff Bada identified that aspartic acid was racemizing much more rapidly than isoleucine was epimerizing, offering an opportunity to date much younger fossils. Bada and coworkers applied this method to the dating of fossil bones and to the determination of past temperatures, by measuring the extent of racemization in several radiocarbon-dated bones. Hare worried that bone lost proteins too rapidly to be reliable, but so (to a lesser extent) did shell (Wehmiller 1977; Masters and Bada 1977, 1978; Miller and Hare 1980; Hare 1988). High profile studies, while the method was still under development (the sites of Boxgrove (Bowen and Sykes 1994); and del Mar (Bada et al. 1974, 1984)), resulted in controversial age estimates which led to a loss of support to the technique in parts of the community (Marshall 1990).

Studies on the mechanisms of racemization and pioneering applications of the method to archaeological and geological contexts (including meteorites, e.g., Engel and Nagy 1982) continued through the 1980s, the 1990s, and the 2000s. The application of AAR dating was mainly as a relative dating tool to identify the age of different geological deposits: aminostratigraphy (Miller et al. 1979). Research in this area continued, driven by a small number of groups, mainly in the USA, for example, Giff Miller, Darrel Kaufmann, and Glen Goodfriend working in the high Arctic and elsewhere (Miller et al. 1983; Goodfriend 1991, 1992; Kaufman and Brigham-Grette 1993; Kaufman and Sejrup 1995; Goodfriend et al. 1996) and John Wehmiller dating shell horizons along the east and west coasts of the USA (Wehmiller et al. 1977, 1995; Wehmiller 1982, 2013; Kennedy et al. 1982; Rockwell 1992) and South America (Hsu et al. 1989; Rutter et al. 1989). Datasets were also accumulated for China (Oches and McCoy 2001), Australia (Murray-Wallace and Kimber 1987; Murray-Wallace et al. 1993; Miller et al. 1997, 2005), Africa (Brooks et al. 1990; Miller et al. 1999), the Mediterranean (e.g., Hearty et al. 1986), Great Britain and the North Sea (Bowen et al. 1985, 1988; Bates 1993; Meijer and Cleveringa 2009). Many of these datasets are publicly available through the NOAA website, where additional citations can be found, as well as maps showing the scale of some of these AAR investigations. During the same years, scientists such as Ritz-Timme and Ohtani were using the method as a forensic technique to estimate the age of tooth dentine (Ohtani and Yamamoto 1991; Ritz-Timme et al. 2000).

The next turning point in research would then occur when two fields of research, which had been proceeding somewhat in parallel throughout the twentieth century, finally met: studies on protein-induced mineralization of hard tissues and studies on protein diagenesis. This led to the rationalization of the key concepts of intercrystalline versus intracrystalline proteins in biominerals.

Key Concepts

In considering the fate of amino acids in biominerals, it is helpful to operationally define two pools of constituent proteins, inter- and intracrystalline.

Intercrystalline

The intercrystalline fraction is defined as the components which are destroyed by chemical treatment, occasionally reduction with hydrazine (N_2H_4), usually oxidation with sodium hypochlorite, NaOCl (Sykes et al. 1995). As the latter is far more common, this will form the basis of subsequent discussion. The ability to destroy the organic matter implies that it occupies interstices in the biomineral between major contiguous blocks, such that they form a connected network (Suzuki et al. 2011). In biominerals with microcrystals (e.g., bone), all proteins are intercrystalline, as the individual mineral elements are too small to encapsulate proteins. In the case of bone, proteins may be entrapped in mineral aggregates (Salamon et al. 2005), but this has not yet been the focus of geochronological studies.

Intracrystalline

The intracrystalline fraction is that which survives prolonged oxidation/reduction. Since the definition is operational, it leads to a number of issues: the concentration of the oxidant, the duration of the treatment, and the optimal particle size need to be tested for each biominerals. Prolonged exposure to bleach causes a slow but steady decline in amino acid concentrations and an increase in racemization, indicating that the system is not perfectly isolated. The operational definition usually refers to crushed biomineral (around 500 μm particle size) exposed to 12 % wt/vol NaOCl for 48 h (Penkman

et al. 2008). The effect of oxidation with NaOCl (bleaching) is shown schematically in Fig. 2: the bleach removes the intercrystalline proteins, more prone to contamination and interaction/exchange with the environment. The protected intracrystalline fraction contains both the original proteins and their degradation products. This enables the quantification of the extent of protein breakdown occurring via different reactions: peptide bond hydrolysis and amino acid racemization and decomposition (e.g., dehydration of the amino acid Ser to Ala).

Within the intercrystalline fraction, the extent of retention of amino acids will be a function of the degree of protein breakdown, the rate of loss from the sample, and any contribution from the burial environment itself. Therefore, there will be a broad correlation between the age of the sample and the extent of racemization, and local burial conditions will dictate the overall value. The intracrystalline fraction should behave in a more predictable fashion (Sykes et al. 1995). In the burial environment, the intercrystalline proteins are often lost quickly, and therefore, many past studies that were analyzing whole-shell proteins were *effectively* analyzing the intracrystalline fraction. Therefore, the isolation of this fraction through chemical pretreatment is more important for samples with a short burial history. The added advantage of bleaching is the removal of external contaminants, e.g., exogenous amino acids. However, the effectiveness of bleaching needs to be tested for each

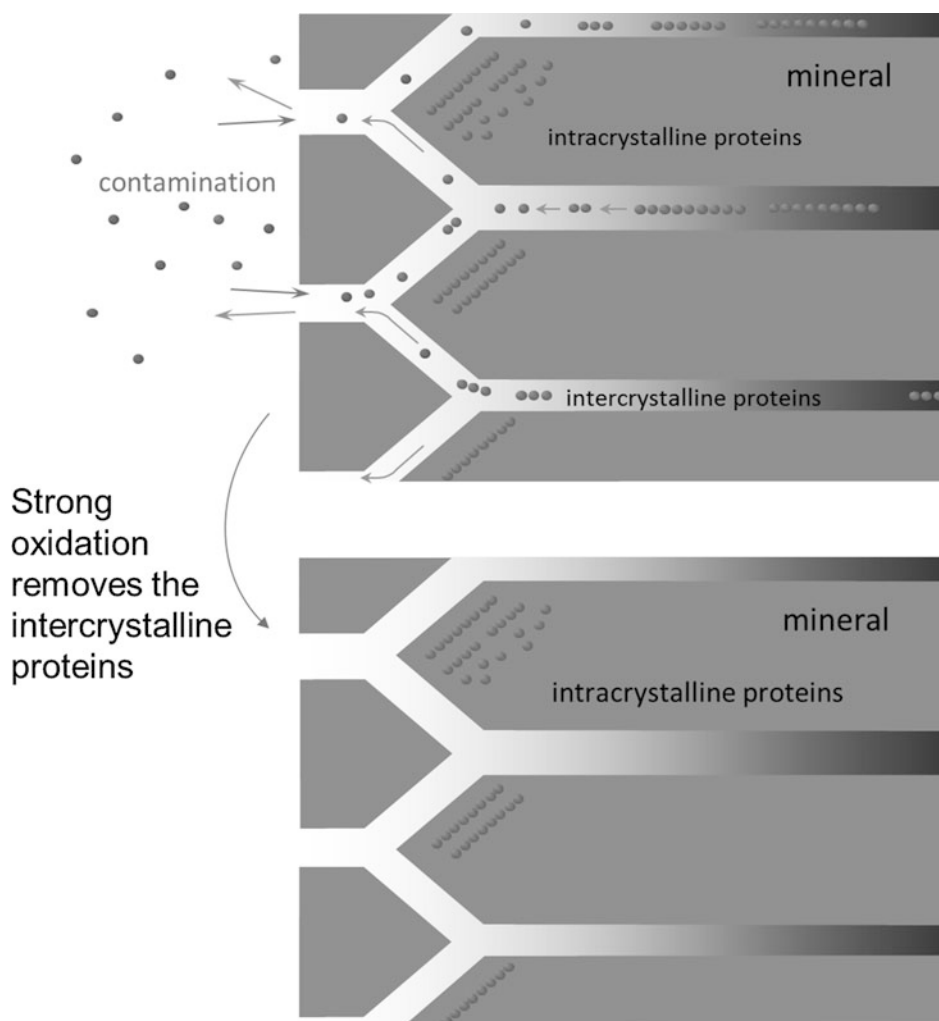


Fig. 2 A strong oxidation treatment is able to remove the intercrystalline protein from biominerals, leaving behind a fraction of the original proteins, degraded in situ (effectively, in a closed-system environment)

biomineral: for example, the isolation of the intracrystalline proteins from the chitin-rich ostracod valves has been shown to be not straightforward (Bright and Kaufman 2011). Nonetheless, the conceptualization of the intracrystalline fraction has added a further piece to the jigsaw, along with other experimental evidence on the behavior of proteins in biominerals (high-temperature experiments, intergeneric comparisons, and diagenetic models, e.g., Wehmiller 1980; Mitterer and Kriausakul 1984). Subsequent discussion will refer to racemization analysis of the intracrystalline fraction, unless otherwise explicitly stated.

The Life and Death of a Protein: From Biomineralization to Breakdown

Although the presence of water trapped in mollusk shell carbonates had already been noted (Hudson 1967), for many years, the idea of the intracrystalline proteins seemed to make little sense, even when the first detection of organic material and water trapped within the crystals was reported: a so-called “frothy” structure in single crystals of *Mytilus* nacre (mother-of-pearl) was observed by transmission electron microscopy (TEM; Towe and Thompson 1972).

Why are proteins trapped inside crystals? Decades of research in biomineralization is starting to unveil the process of entrapment of proteins within biominerals. Fast-forming systems, such as eggshell, retain higher concentrations of amino acids in the intracrystalline fraction than slow-forming systems, for example, mollusk shells, and therefore in part incorporation may be kinetically driven. Ostrich eggshell retains ~30 nmol amino acids per mg mineral after bleaching; limpet shells (*Patella vulgata*) a mere ~4 nmol per mg. However, both biominerals contain ~50 nmol amino acids per mg of unbleached (i.e., intracrystalline + intercrystalline) biomineral (Crisp et al. 2013; Demarchi et al. 2013a). Importantly, the intracrystalline proteins and, generally, proteins in biominerals display a wide range of amino acid sequences and three-dimensional structures (these can be found in the NCBI database).

Proteins promote and regulate biomineralization. The model proposed for the chicken eggshell protein ovocleidin-17 (OC-17) (Freeman et al. 2010) highlights the role of Arg-rich domains of the protein and their action as “clamps” that bind calcium and promote the transformation from amorphous calcium carbonate (ACC) to crystalline mineral. If these crystallites aggregate to form mesocrystals (Cölfen and Antonietti 2005), it is easy to envisage how the protein becomes surrounded and entrapped. However, even in situations in which the protein does not act as a catalyst, other authors have proposed models where remnant proteins are overgrown into the mineral (Li et al. 2011; Okumura et al. 2013). The role of these in modifying the structural properties of the mineral is now indeed an active area of research (e.g., Okumura et al. 2013).

Whole-genome sequencing and targeted analysis, such as by immunohistochemistry, are beginning to reveal the differences in the character of proteins found in biominerals, and the new sequences and new tools for analysis are rapidly accelerating knowledge of these systems. One example is the intriguing set of glycine-asparagine (Gly-Asn or, in one-letter code, GN) repeats found in the sequence of the protein N16.1 isolated from the intracrystalline fraction of the mollusk *Pinctada fucata* (see Table 1).

The Gly-Asn repeat is highly unstable and degradation rates depend upon environmental temperature; therefore, this might suggest that variants of this organism which are biomineralizing at different conditions (e.g., water temperatures) might have evolved a system whereby they increase the number of the GN repeats to enhance the stability of the protein. From this brief review, it is evident that we are only beginning to understand the role played by the intracrystalline fraction; some may be accidental overgrowth, others may be trapped catalysts, while still others may be

Table 1 Gly-Asn repeats are found in the sequence of intracrystalline proteins isolated from *Pinctada*

Start position	Sequence	End position	Protein name
80	FYYMCCYTDDD-NGNGDGNGNGFNLYKSLYGGYGNGNG	116	MA162_PINFU
80	FYYMCCYTDDD-NGNGNGNGNGFNLYKSLYGGYGNGNG	116	MA165_PINFU
80	FYSLCCYTDDD-NGNGNGNGNGFNLYKSLYGGYGNGNG	116	I7GQ94_PINFU
80	FYSLCCYTDDD-NGNGNGNGNGNGLNYLKSLYGGYGNGNG	118	L8B660_PINFU
80	FYSLCCYTDDD-NGNGNGNGNGNGLNYLKSLYGGYGNGNG	118	MA161_PINFU
80	FYSLCCYTDDD-NGNGNGNGNGNGLNYLKSLYGGYGNGNG	118	MA163_PINFU
81	YYTLCCYTEDD- NGNGNGNGNGYGNGNGNGNGNLYLKYLFGGNGNGNG	127	MAPE_PINMG
81	YYTLCCYTDDD- NGNGNGNGNGYGNGNGNGNGNLYLKYLFGGNGNGNG	127	MA14_PINMA

playing a functional role, perhaps even acting as remote triggers controlling later-phase processes. What we are beginning to understand is that the entrapped intracrystalline proteins are not homogeneous and it is therefore not surprising that their rates of decomposition (and thus their rate of racemization) will vary from species to species and ultrastructure to ultrastructure, the so-called species effect (Lajoie et al. 1980; Wehmiller 1980), which is widely observed in AAR. Indeed, many whole-shell AAR studies recognized the presence of different peptide fractions, some more refractory than others (e.g., Kaufman and Sejrup 1995), and this was used as a tool for taxonomic identification (Andrews et al. 1985; Wehmiller 1989; Kaufman et al. 1992). What is more surprising is perhaps the fact that the species effect is preserved within the intracrystalline fraction and a common “template” cannot be found, although these proteins are likely to be directly involved in the interaction with the mineral phase.

Death and Diagenesis

After deposition, organic remains are in thermodynamic disequilibrium with their environment and they will attempt to reach equilibrium with the surrounding environment. The sequence of intermediate metastable conditions is defined as a series of diagenetic pathways or diagenetic trajectories (Wilson and Pollard 2002). Several difficulties arise in defining these for protein diagenesis, even when looking at the intracrystalline fraction, because (a) the actual amino acid sequence (and composition) for most proteins is unknown and (b) the temperature sensitivities of each of the reactions within the network of reactions driving the overall diagenesis are difficult to assess. Therefore, a “black box” approach is used in protein diagenesis studies, where three main reactions, occurring simultaneously, are tracked, as they can provide information on the time elapsed since degradation started, i.e., the time of death of an organism.

Hydrolysis

Peptide bonds are inherently unstable and will undergo hydrolysis, the rate depending upon a number of factors: the pH of the solution, the presence of catalysts, the availability of water (which is consumed in the reaction), and the steric constraints upon the bond. One advantage of the

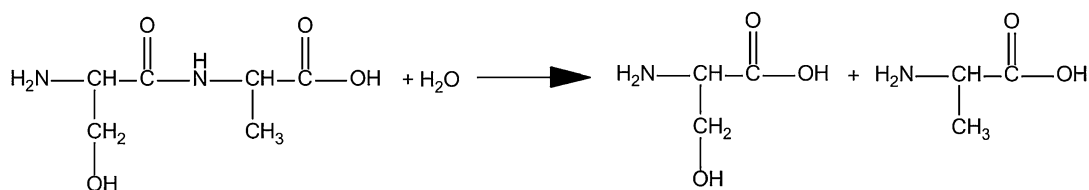


Fig. 3 Mechanism of dipeptide hydrolysis

intracrystalline fraction is that all of the above factors should be equivalent in the tissues of the same taxon.

Hydrolysis breaks the peptide bonds, yielding progressively shorter peptides until only the basic building blocks, the free (as opposed to peptide-bound) amino acid residues, are present. Hydrolysis requires the presence of chemically available water (Fig. 3), which must be present in the intracrystalline fraction, since (a) we observe the rapid release of amino acids from the peptide-bound fraction into the free amino acid pool due to peptide bond hydrolysis and (b) it has been directly observed within crystallites (Hudson 1967; Gaffey 1988). Furthermore, diagenetic decomposition of hydroxy amino acids, Ser, Thr, and Glu (Bada et al. 1978; Walton 1998), and carbohydrates (Collins et al. 1992) would increase the amount of water available for hydrolysis of the intracrystalline proteins. However, a residual un-hydrolyzed fraction is usually found within the intracrystalline fraction of different biominerals; Collins and Riley (2000) speculated that this could be due either to a reduction in the availability of water or to the presence of a recalcitrant pool of amino acids.

Each protein possesses a unique primary structure and contains a wide variety of peptide bonds of different strengths. However, hydrolysis exhibits a certain degree of specificity, and in the natural environment, under mild pH and temperature conditions, three main mechanisms of hydrolysis are likely to occur (Bada 1991):

1. Cleavage of internal peptide bonds, which is rapid for Ser, Ala, Gly, and Thr and slowest for Val and Ile.
2. Internal aminolysis at the N-terminus, yielding diketopiperazine (cyclic dipeptides); this is more rapid than internal cleavage for small peptides made up of hydrophobic amino acids and at neutral pH. The importance of this reaction therefore increases with increasing extent of diagenesis.
3. Hydrolysis of an amino acid at the C-terminus, which is acid/base catalyzed but is independent of pH between pH 5 and 9 (Kahne and Still 1988). The importance of this reaction also increases with proceeding diagenesis.

The overall extent of hydrolysis in fossil biominerals is a useful proxy of the age of the sample and can be easily quantified as the percentage of free amino acids (FAA) over the total hydrolyzable amino acids (THAA): $\% \text{FAA} = [\text{FAA}]/[\text{THAA}] \times 100$.

The temperature sensitivity of peptide bond hydrolysis is dependent on the relative stability of the bonds between pairs of amino acids; overall, studies into the extent of hydrolysis at high temperature (during laboratory simulations of diagenesis or kinetic experiments) have shown that, generally, the apparent activation energy for hydrolysis is lower than for racemization (Crisp et al. 2013; Demarchi et al. 2013b; Tomiak et al. 2013). This implies that at lower (burial) temperatures, hydrolysis will be favored over racemization and that therefore hydrolysis represents the rate-limiting pathway for overall diagenesis. Indeed, hydrolysis is a key reaction step in racemization as it generates N-terminal residues, and these are the most prone to undergo racemization (Fig. 4).

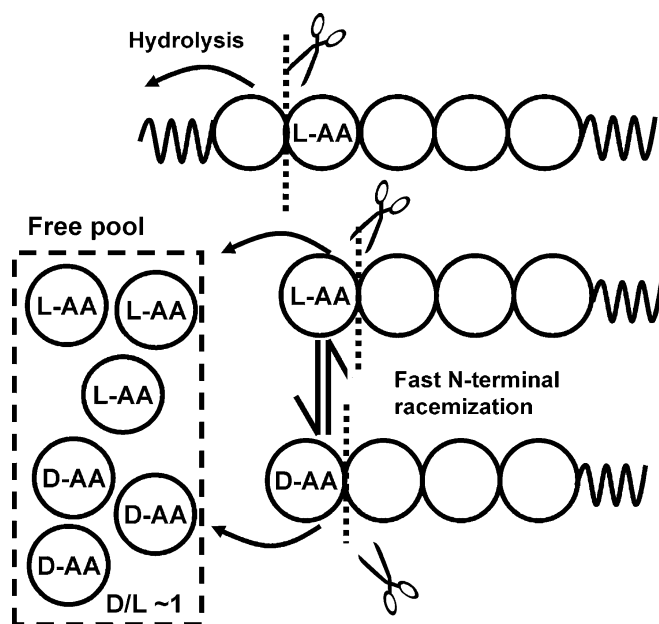


Fig. 4 Schematic mechanism of peptide bond hydrolysis at the N-terminus, promoting fast racemization of amino acids (AA) that are released in the free pool

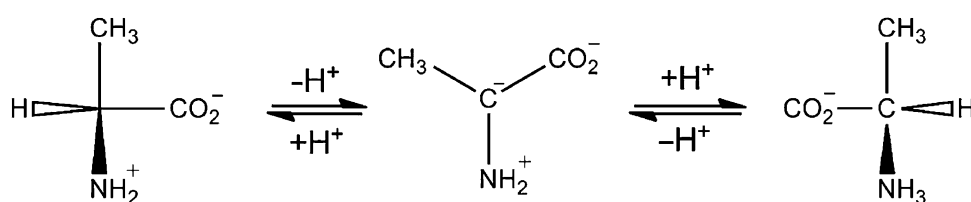


Fig. 5 Proposed mechanism of racemization of free amino acids, via a carbanion intermediate

Racemization

An amino acid can exist in one of four states: (a) entirely bound within a peptide chain, (b) at the N-terminus, (c) at the C-terminus, or (d) as a free amino acid. This influences its ability to undergo racemization.

Free Amino Acids

The main focus of attention has traditionally been on the mechanisms of racemization of free amino acids in aqueous solution; Neuberger (1948) proposed that abstraction of the hydrogen linked to the central carbon leads to the collapse of the tetrahedral geometry of the amino acid and the formation of a planar carbanion. This is equally likely to be attacked by a proton from either direction, with the possibility of umbrella-like inversion of the tetrahedron, thus regenerating the L-form or producing the D-enantiomers (Fig. 5). The rate-limiting step of the reaction is therefore the abstraction of the proton. Increasing the electron-withdrawing and resonance-stabilizing capacities of the substituents attached to the central carbon of an amino acid causes a corresponding increase in the racemization rate (Bada and Schroeder 1975). The mechanism is applicable not only to free amino acids but also to amino acids bound in peptides and proteins: if the amino group is protonated (as it would be at an N-terminal position), then it is able to participate in resonance, facilitating the loss of the hydrogen.

Different amino acids display different relative racemization rates: since racemization is enhanced by species which are able to stabilize the carbanion intermediate, a major role is played by the –R group. For example, amino acids that have –R groups which are highly electron withdrawing (e.g., Ser) should have the fastest racemization rates at neutral pH, while those which have substituents that are electron donating (e.g., Val) should have the slowest rates (Bada 1985). Since the –R group is amino acid specific, each amino acid is characterized by a different value of enthalpy and entropy, which reflect the electronic and steric factors determining racemization rates for free amino acids in aqueous solution. Although different factors enhance or retard the racemization rates, racemization of free amino acids in aqueous solution has generally been found to obey first-order reversible kinetics (Bada and Schroeder 1975):

$$\ln[(1 + D/L)/(1 - D/L)] - \text{constant} = 2kt \text{ (for amino acids with one chiral centre)}$$

$$\ln[(1 + A/I)/(1 - K'(A/I))] - \text{constant} = (1 + K')k_{\text{Ile}}t \text{ (for Ile)}$$

where t is time and the constant term is different from zero as it represents the small amount of D-enantiomer produced during sample preparation; $K' = 1/K_{\text{eq}}$ and K_{eq} is the equilibrium alloisoleucine/isoleucine (A/I) ratio, which is ~1.3 to 1.4 (Bada and Schroeder 1975).

These equations can be used for deriving the racemization rate of a given free amino acid in aqueous solution at a known temperature. Typically, kinetic experiments are conducted at three (or more) different temperatures and the increase in D/L value monitored over time. When the experimentally derived $\ln [(1 + D/L)/(1 - D/L)]$ is plotted against the time of isothermal heating, if the reaction is first order, then a linear relationship is found, of slope $2k$. The intercept represents the constant value, i.e., the preparation-induced racemization. The racemization rates obtained at the three (or more) temperature points can then be used for extrapolating the racemization rate at any temperature. This is possible because the reaction rate and the temperature are directly related in the Arrhenius relationship:

$$k = Ae^{(-E_a/RT)}$$

where k is the rate constant, A is the frequency factor (year^{-1}), E_a is the activation energy (kJ/mol or kcal/mol), R is the gas constant (0.001987 kcal/mol or 0.008314 kJ/mol), and T is the absolute temperature (degrees Kelvin, K). A plot of the natural logarithm of k versus $1/T$ yields a straight line of slope E_a .

In the real world the situation is more complex, because unlike free amino acids, the extent of racemization is a consequence of a number of reactions, notably hydrolysis and racemization, with different temperature dependencies, which means that net racemization rates are unlikely to display a perfect linear relationship with temperature. By estimating the activation energy and the frequency factor, the racemization rate at the burial temperature for fossil samples of unknown age can be approximated. The temperature value used for fossil samples is the “effective diagenetic temperature” (EDT; see “► [Amino Acid Racemization, Paleoclimate](#)”) representing the integrated effect of all temperatures to which the samples at a given depth have been exposed (Wehmiller 1977).

Bound Amino Acids

Racemization of peptide-bound amino acids occurs via complex pathways, which have not yet been fully clarified. The body of knowledge acquired in the past decades by experimenting on both synthetic peptides and biominerals has allowed building a general model (Wehmiller 1980; Mitterer

and Kriausakul 1984) whereby it is postulated that peptide-bound amino acids are unable to racemize until progressive hydrolysis drives them to a terminal position (Fig. 4). However, exceptions to this general rule are the fast in-chain racemization of Asn and Asp (Geiger and Clarke 1987) and Ser (Demarchi et al. 2013c) and the accelerated rate of racemization in diketopiperazines (Steinberg and Bada 1981) at the peptide chain C-terminus. In general, the rate of amino acid racemization within a protein retained in a closed system depends on (a) the temperature of the environment (or of the experiment), (b) the availability of water for peptide bond hydrolysis, (c) the position of the amino acid within the protein sequence throughout diagenesis, and (d) the three-dimensional structure of the protein.

Therefore, kinetic relationships derived from high-temperature experiments are unable to capture the underlying chemical rationale of the mechanisms involved in peptide-bound amino acid racemization. Mathematical expressions have been developed that enable the calculation of *apparent* racemization rates and the assessment of the temperature dependence of the reactions and, ultimately, the extrapolation of an absolute age. These equations (first order, parabolic, power transformations; Clarke and Murray-Wallace 2006) are usually derived from high-temperature experiments on biocarbonates, and these can be further constrained by the measurement of racemization in samples of well-defined age, for example, on radiocarbon-dated shells. This then allows building a calibrated age equation (e.g., Kosnik et al. 2008, 2013) that can be used effectively to derive age since death for subfossil biominerals. This is important, as studies on the intracrystalline fractions of avian eggshell, mollusk shells and corals have shown clearly that the pathways of diagenesis at high temperature may not necessarily be the same as those at low temperatures (Crisp et al. 2013; Demarchi et al. 2013b; Tomiak et al. 2013); therefore, the age-racemization relationship must be calibrated for samples of known age and where the effective diagenetic temperature can be reconstructed (e.g., foraminifera from deep-sea cores). This is further confirmed by the recent study of Allen et al. (2013), who fitted a variety of different functions to racemization data and observed that high-temperature and field data behave differently. In part, this is because the relatively high activation energies (~120 kJ/mol) mean that unless the temperature range is very narrow, data usually covers different stages within the decomposition pathway. Because of this, an alternative approach, which estimates rate differences simply by relative scaling, has been proposed (the so-called “model-free” approach; Crisp et al. 2013; Demarchi et al. 2013b; Tomiak et al. 2013).

The temperature sensitivity of the reaction is especially important when considering the calibration of samples over Pleistocene timescales: temperature fluctuations affect the rates of racemization, and therefore, the succession of glacial and interglacial stages needs to be considered (a recent example of combining kinetic models and age calibration (by $^{87}\text{Sr}/^{86}\text{Sr}$) over the Quaternary is the study by Wehmiller and colleagues (2012) in the US mid-Atlantic Coastal Plain).

Methodology

Sample Types

In order to use a substrate for dating, the researcher has to be confident that the material will prove suitable, i.e., that the biominerals will have retained its original proteins. These would have been degrading at a certain rate, depending upon the proteins themselves (and therefore the species effect; Lajoie et al. 1980), the pH of the environment, and the burial temperature. Biominerals, such as eggshell, mollusk shells, foraminifera, brachiopods, ostracods, corals, and tooth enamel, are all good substrates for AAR dating.

When looking at intracrystalline proteins, the most common problem associated with AAR dating is that the system is partially reset if the biomineral undergoes diagenetic alteration, resulting in the opening up of a previously closed system. Due to the difficulty of identifying diagenetic transformation from aragonite to calcite, the latter biomineral is favored. A comparison of the aragonitic shells and calcitic opercula of *Bithynia tentaculata* (and *Bithynia troschelii*) highlighted the limitations with the former: in the case of the calcitic opercula, some samples displayed evidence of distortion and recrystallization, and these too displayed atypical patterns of racemization (Penkman et al. 2007, 2013). However, this does not mean that aragonitic shells should not be used: the presence and extent of diagenetic alterations can be characterized by microscopical observations and techniques such as X-ray diffraction, and the use of multiple samples of different taxa is important for recognizing aberrant results.

Sample Collection

The best way to collect samples for AAR is to collect as many as reasonable, to note all information available and, whenever possible, to define the sampling strategy with the scientists in charge of the excavation of the site. Details on sample collection strategies can be found in many studies and are summarized in Wehmiller and Miller (2000). If collecting in the field, note the depositional environment and the position of the specimens, especially when dealing with high-energy depositional environments, with high likelihood of age mixing (e.g., Wehmiller et al. 1995; Krause et al. 2010).

If collecting from a museum, the information on sample collection and storage may not always be available. This is important because one of the major issues to be taken into account is whether the samples have been exposed to conditions that have impacted on their thermal history, increasing the levels of racemization: for example, drying in an oven or exposure to heat during shallow burial. If possible, avoid sampling from the surface of an outcrop, but target instead samples that are buried under at least 1 m of sediments (or at a depth where the seasonal temperature variations are dampened to less than 6 °C (Wehmiller and Miller 2000)). Burning and heating, especially for edible mollusks or eggshells, should also be taken into account when collecting samples from archaeological sites, e.g., shell middens, or cave deposits in proximity to hearths. Some useful “burning indicators” can be identified on the basis of the bulk amino acid composition and the covariance of D/L values of different amino acids (e.g., Brooks et al. 1991; Miller et al 1999; Demarchi et al 2011; Crisp 2013).

Due to the intergeneric differences in racemization rates, aminostratigraphies can only be built for monogeneric samples; therefore, whenever possible sample multiple taxa from each geological or archaeological unit. At least five individual samples should be taken from each depositional horizon (in both geological and archaeological settings) and taxon, in order to assess the natural variability (Miller and Brigham-Grette 1989) within the taxon and the site.

How Can Amino Acid Racemization Be Measured?

Any mixture of analytes needs to be separated into its individual components in order to achieve quantification. The classic separation technique for complex mixtures is chromatography. Analysis of chiral amino acids is challenging, because the two molecules (L- and D-enantiomers) are only subtly different. Broadly, three different strategies have been used. Originally, diastereomers were measured using ion exchange chromatography, which could be followed by a variety of different (some very sensitive) detection methods. The method had the advantage of being robust, sufficiently

so for Ed Hare and his team to develop a system that could be taken to the field. However, it had one major disadvantage: it could only discriminate between the two diastereomers of isoleucine, one of the slowest-reacting amino acids.

A new method of gas chromatography (GC), first developed at NASA-Ames, became routinely used during the 1970s (see the first interlaboratory comparison study led by Wehmiller in 1984). This guaranteed very good separation of the constituent amino acids separated on a chiral stationary phase (column), and although more challenging than others, its extremely good separation of multiple amino acids has meant that GC methods are still used, notably by some forensic laboratories who demand the very best separation and resolution, for example, when assessing very low levels of racemization in young (forensic) samples (Ohtani and Yamamoto 1991; Ritz-Timme and Collins 2002).

In 1998 Kaufman and Manley published a key paper in which they used a chiral derivative (based upon chemistry previously developed by Brückner et al. (1991)) to separate nine enantiomeric pairs on a conventional HPLC (high-pressure liquid chromatography) reverse phase column (Kaufman and Manley 1998). This RP-HPLC method is very sensitive, paving the way for high-throughput applications of the technique; scientific AAR studies now commonly report hundreds of analyses. This is now the most widely applied method, although alternatives (e.g., UHPLC, ultrahigh-performance liquid chromatography) are being considered to enhance the sensitivity and the speed of the analyses, in order to further reduce sample size and increase throughput. Published interlaboratory comparison studies (Wehmiller 1984, 2013; Powell et al. 2013) detail the different characteristics of each method.

Present Investigations and Future Directions

If suitable samples and suitable separation techniques are used, AAR can be a very powerful dating tool. The most successful application of the technique is perhaps in assessing the age of microorganisms (e.g., foraminifera tests) in deep-sea cores, where the temperature is stable and the variability reduced (e.g., Müller 1984; Kaufman et al. 2008). In the Quaternary record, applications include building calibrated geochronological frameworks for the UK (e.g., Penkman et al. 2013) and sequences in the USA (e.g., Wehmiller 2013) and in the Mediterranean (e.g., Hearty et al. 1986). Great attention has been given to establishing long and precise sequences for the Holocene, e.g., in Australia (e.g., Kosnik et al. 2013). Calibration of the D/L values is obtained through radiocarbon, but advances in luminescence dating and cosmogenic nuclides dating are likely to be in the spotlight of research in the next decade.

Currently, AAR cannot be applied as a numerical method per se, because of a) uncertainties associated with the temperature history of each sample (especially for the Quaternary record at midlatitudes) and b) difficulties in assessing the kinetic parameters of each diagenesis reaction. Paleotemperature models are however becoming more and more sophisticated (see “► [Amino Acid Racemization, Paleoclimate](#)”) and are likely to offer the unprecedented opportunity of refining our understanding of the temperature- and age-driven diagenesis reactions. This, combined with growing information on protein sequence and structure, will likely transform the way AAR scientists think and apply the technique. A greater emphasis on interlaboratory trials (Wehmiller 1984; Powell et al. 2013; Wehmiller 2013) is further evidence of the growing maturity of the discipline.

Acknowledgments

We are truly indebted to two anonymous reviewers for their comments on this manuscript. Their insight in the earlier phases of development of the technique, which they were willing to share with us, has been of invaluable help in compiling this review. The responsibility for any errors or inaccuracies still present is entirely ours.

Kirsty Penkman and the AAR group in York are thanked for their help, support, and discussion over the years.

Cross-References

- ▶ [Amino Acid Racemization, Arctic Environment](#)
- ▶ [Amino Acid Racemization, Biostratigraphy](#)
- ▶ [Amino Acid Racemization, Coastal Sediments](#)
- ▶ [Amino Acid Racemization, Egg Shell](#)
- ▶ [Amino Acid Racemization, Eolianites](#)
- ▶ [Amino Acid Racemization, Fluvial and Lacustrine Sediments \(AAR\)](#)
- ▶ [Amino Acid Racemization, Loess and Glacial Sediments \(AAR\)](#)
- ▶ [Amino Acid Racemization, Marine Sediments](#)
- ▶ [Amino Acid Racemization, Paleoclimate](#)
- ▶ [Biostratigraphy](#)
- ▶ [Chromatography](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Luminescence Dating](#)
- ▶ [Radiocarbon Dating](#)
- ▶ [Magnetostратigraphic Dating](#)
- ▶ [U-Series Dating](#)

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Amino Acid Racemization, Paleoclimate

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Definitions

Amino acid racemization (AAR): changes in the chirality of amino acids, the building blocks of proteins, resulting from the time-and-temperature-driven breakdown of proteins. AAR is used in the geosciences as a relative dating technique, typically comparing the ratio of D/L amino acid enantiomers in biominerals.

Paleoclimate: the complex interrelated changes brought upon by temperature shifts caused by orbital forcing of the geosphere, hydrosphere, atmosphere, biosphere, and anthroposphere throughout Earth's history.

Introduction

The level of racemization in any one sample is in effect a measure of the integrated time/temperature history (thermal age) that accounts for the observed degree of protein diagenesis. Therefore the contribution of amino acid racemization (AAR) to understanding past climate changes is twofold: it can be used either as a geochronological tool, to reconstruct the timing of major climatic events, or (less commonly) as a paleothermometer in the case of samples of known age, because the higher the observed rate of racemization (k , see Arrhenius plot in Fig. 1), the warmer the burial history.

Dating Past Climate Cycles

AAR geochronology can help to clarify the timing of past climatic cycles and the extent of the environmental responses to these changes, from a local to a global scale. One of the most successful applications is the identification of interglacial episodes in the patchy terrestrial sedimentary record, which can thus be linked to the global temperature fluctuations recorded in ocean and ice cores (Oxygen Isotope Stages or Marine Isotope Stages). This is particularly effective at high latitudes, where cyclic fluctuations in global temperature have resulted in the accumulation of sediments typically during warm ice-free periods; here AAR can help to assign these deposits to specific climate cycles (Penkman et al. 2013). In these and in other midlatitude regions, models have been developed that link the acceleration of the racemization rates to interglacial temperature increase and sea-level highstands (e.g., Hearty et al. 1986).

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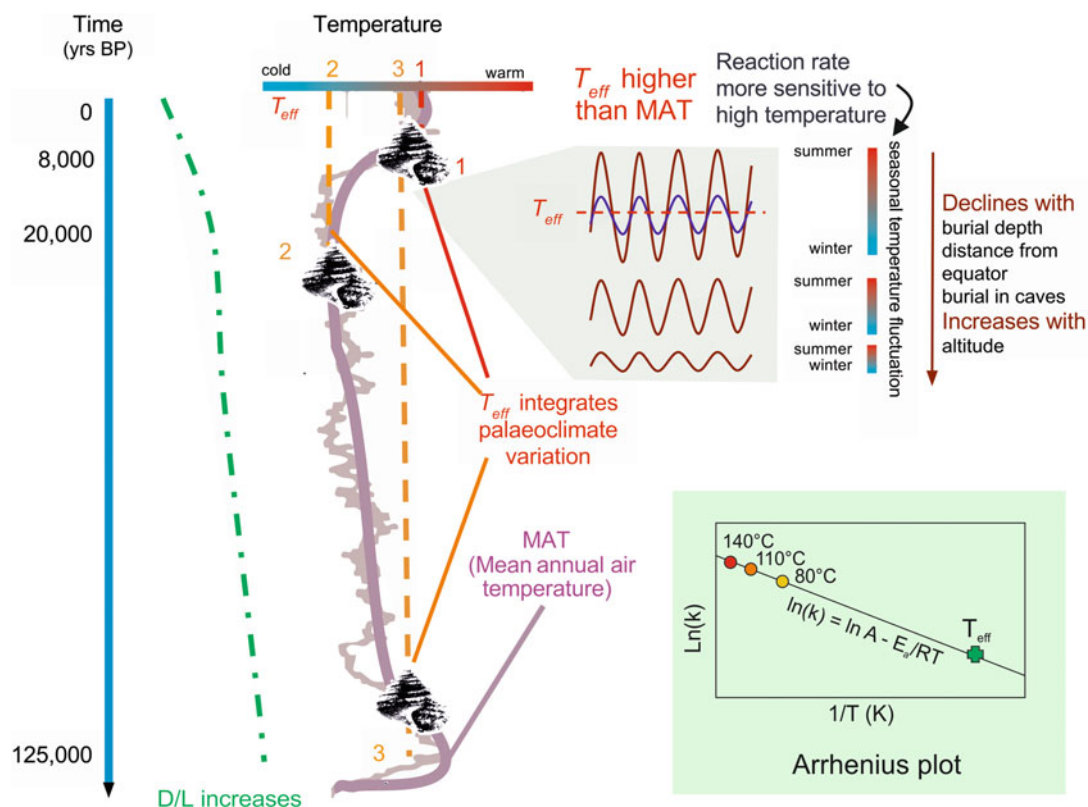


Fig. 1 Increase in the extent of racemization as an effect of time and temperature, e.g., throughout the last glacial/interglacial cycle

Paleothermometry

The rates of protein decomposition (diagenesis) increase exponentially with temperature. Effective burial temperature (T_{eff} , also known as the effective diagenetic temperature or EDT (Wehmiller 1977)) is the temperature inferred from rate constants determined in dated samples (Fig. 1). This is influenced by (i) seasonal temperature fluctuations (which increase with distance from the equator but are dampened with burial depth and shading) and (ii) long-term changes in global temperature.

Paleothermometry and AAR are therefore inextricably entwined. Accurate age estimates can be obtained on the basis of D/L values, when the temperature history (T_{eff}) of a sample is known; conversely, when the absolute ages of the sample are known, T_{eff} can be calculated. In both cases the kinetic parameters of the reaction must be established (usually estimated from higher temperatures using an Arrhenius plot; see Fig. 1). Age estimations are more likely to be more accurate where the extent of seasonal fluctuation is minimized (e.g., sediment cores), since near-surface sediments (especially deposits of anthropogenic origin, e.g., shell middens) may experience short-lived periods of extreme temperature.

The accuracy of the estimates of the kinetic parameters affects these calculations (McCoy 1987); kinetic models based on high-temperature (artificial) diagenesis (Fig. 1, Arrhenius plot) can only be constrained to the “real” burial temperatures using samples that can accurately be dated by independent means. This is often done using radiocarbon, hence covering the Holocene and Marine Isotope Stages 2 and 3. The disparity between Holocene T_{eff} and that of the sample can be used to estimate changes in paleotemperature (ΔT) at the site, for example, to quantify the extent of cooling during the Last Glacial (e.g., Miller et al. 1987, 1997). If multiple samples of known age are

available, it is then possible to impute a paleotemperature record, but only relatively few attempts have been made to do this due to the need for long, high-resolution chronologies (Kaufman 2003).

Conclusions

Individual biominerals can be considered as temperature loggers which report a single (integrated) thermal age. Improvements in our ability to model paleotemperature mean that in the future it should be possible to predict the thermal history of a specific site at a specific burial depth; an example where this is being attempted is the <http://thermal-age.eu> website. When combined with good kinetic estimates of protein decomposition, it may be possible to use such models to estimate the absolute age of a sample from AAR (or indeed other temperature dependent data, such as hydration of silicates).

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Laser Ablation Inductively Coupled Mass Spectrometer (LA ICP-MS)

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Laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) is an in situ analytical instrument that is used for determining the elemental and isotopic composition of micrometer-sized areas of solid materials such as minerals, glasses, metal alloys, bones, teeth, calcareous shell and wood, and fluids trapped as inclusions within solids (Sylvester 2008). A laser ablation system is connected to an inductively coupled plasma mass spectrometer. Laser pulses remove small volumes of the sample, typically from pits that are 30–50 μm wide and deep, during 1–2 min of ablation. The ablated aerosols are transported in a carrier gas stream to the ICP and converted to ions, which can be separated based on their mass to charge ratios by a mass spectrometer and measured with a detector. The ICP is hot ionized argon gas produced at the tip of a glass torch by an intense electromagnetic field generated by an oscillating current in a water-cooled copper coil wrapped around the glass torch (Linge and Jarvis 2009). Most commonly, the mass spectrometer consists of a quadrupole mass filter or a magnetic sector field mass analyzer incorporating single or multiple collectors (MC). The detector in single-collector instruments is typically a secondary electron multiplier, whereas multiple Faraday cups can be used in MC devices. The moderate capital cost, robust design, multielement capability, short analysis times, minimal sample preparation requirements, and good precision and accuracy of LA-ICP-MS compared to competing techniques for in situ micrometer-scale, chemical analysis have led to its widespread use in university, government, and industry research laboratories worldwide.

For analysis, the sample surface is commonly prepared as a thin polished slice or slab, and imaged using optical light or scanning electron microscopy, in order to select areas appropriate for laser sampling. The sample is ablated in an airtight sample cell flushed with helium gas to transport the ablated aerosols through plastic tubing to the ICP. Ablation is usually carried out using a nanosecond pulsed laser, emitting ultraviolet light, which is absorbed more completely than infrared light by many minerals and other materials, particularly those that are transparent or poor in iron. Most modern systems are based on a neodymium-doped yttrium aluminum garnet (Nd:YAG) solid-state laser using the frequency-quintupled 213 nm output or an argon-fluoride (ArF) excimer gas laser using its fundamental 193 nm wavelength. Recently, femtosecond pulsed lasers have been shown to produce aerosols with smaller particle sizes and negligible sample melting at the ablation site, improving analytical performance (Shaheen et al. 2012).

LA-ICP-MS is used for scientific dating largely by measuring the ages of minerals containing uranium or thorium, which decay to radiogenic isotopes of lead. Zircon is the mineral dated most commonly using the technique, although U-Th-Pb ages for other minerals, such as monazite, baddeleyite, allanite, apatite, rutile, and titanite are increasingly reported. Minerals with ages from as young as about a million years to those that comprise the oldest known material found in meteorites can be dated by LA-ICP-MS using the U-Th-Pb method. Ages are commonly reported with uncertainties of 1 % or less, but interlaboratory comparisons have documented biases of about 2 % (Košler et al. 2013). The major source of error in U-Th-Pb dating by LA-ICP-MS is inaccurate

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correction for laser-induced fractionation of more-volatile Pb relative to more-refractory U and Th. U-Th/Pb fractionation is matrix dependent and is affected by variations in laser sampling as a function of mineral composition, color, crystallinity, and fracturing. Various procedures are employed to limit U-Th/Pb fractionation including matching calibration standards to the matrix of the unknowns, ablating with lasers emitting deep ultraviolet (193 nm) light or femtosecond pulses, moving the sample beneath the laser beam (referred to as raster or scan mode) to limit the depth of ablation, and various mathematical corrections.

Cross-References

- [Mass Spectrometry](#)
- [Secondary Ion Mass Spectrometer \(SIMS\)](#)
- [Uranium-Lead Dating](#)
- [Zircon](#)

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Dendrochronology, Fire Regimes

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Definition

Use of tree-ring data and methods to reconstruct past fire timing, fire regimes, and fire effects on individuals, communities, and ecosystems.

Introduction

Fire directly or indirectly affects woody plants in many ways, some of which will leave evidence in age or growth patterns in individual trees or community structure that can be cross-dated using dendrochronological methods. This evidence can be used to reconstruct past fire dates, fire regimes, and fire effects on individuals, communities, and ecosystems (“pyrodendroecology”). Fire regimes are defined as the combination of fire frequency, severity, size, seasonality, and relationships with forcing factors such as climate or changes in human land use.

Fire Evidence in Trees and Community Structure

A common type of fire evidence is from severe fire that kills all or most trees in an area which opens up space for new trees to establish. Even-aged forest structure is often used as evidence of past lethal fire, also referred to as “stand-replacing” fire. Such evidence provides a minimum date for the fire (i.e., the fire occurred sometime before the innermost dates of the oldest trees), and, by sampling multiple stands in an area, estimates of the fire size can be made based on broader-scale patterns of tree ages. Conversely, multiaged structure is considered to be evidence of less severe fires or other patchy mortality and recruitment events. Note that a dating limitation to age structure studies is that rarely are total tree ages able to be reconstructed. Tree ages are usually derived from increment cores or cross sections collected at a height above and several years after the date of seedling germination. Often cores or sections for age structure studies are collected low on the tree bole (e.g., 10–30 cm above ground level), and some studies have applied a correction factor to estimate germination dates from sample-height pith dates. However, regardless of these methods, generally age structure data are not accurate to exact years of tree germination.

Another commonly used line of evidence of past fire is from fire scars (Fig. 1). Fire scars are areas of cambial mortality resulting mainly from lower intensity fires that burn through surface fuels such as leaf litter, grasses and other herbaceous plants, or shrubs. If the cambium is killed all the way around the tree circumference, the tree is girdled and dies. However, if only a portion of the cambium is killed, a fire scar is formed and the tree continues to live. The formation of a fire scar is

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Fig. 1 (Left) A *Pinus ponderosa* stump with a fire-created “catface” facing to the right. The catface was formed from repeated fire scars (visible as distinct ridges inside the catface). Bark and sapwood have eroded from the outside of the stump, and only the heartwood is left. The stump was cut with a crosscut saw, placing the date of cutting likely in the late nineteenth or early twentieth century before widespread use of motorized chainsaws. (Right) Cross-section sample cut with a chainsaw from a fire-scarred *P. ponderosa* snag (standing dead tree). Dates of fire scars are marked on the section. The tree died in 1916 from a bark beetle attack as evidenced by blue stain in the small remnant of sapwood visible at the top of the photograph. Most of the sapwood has decayed since the tree died, limiting the amount of time that a death date could be established (Photograph credits: P. M. Brown)

a function of both bark thickness (thicker bark helps to insulate the cambium) and the intensity of the fire (a certain temperature is necessary to kill the cambium through the bark). After scar formation, circumferential growth will continue from the margins of the dead cambial zone, often completely regrowing over the scar unless the area is burned again in a subsequent fire (Smith and Sutherland 2001). After a tree has been scarred once, rapidly growing woundwood on the scar margins tends to have thinner bark making it more susceptible to subsequent fires. Because of this susceptibility, long sequences of multiple fire scars are often found on trees in forested ecosystems that experienced frequent, episodic, low intensity fires, such as many dry *Pinus* ecosystems around the world (Falk et al. 2011; Fig. 1 right).

Fire scars can usually be dated to their exact year of formation within a cross-dated ring series. Fire frequency is derived from sequences of composited fire-scar records found on multiple trees in a stand or study area. Seasonality of burning also can be estimated from the position of the scar within the annual ring and knowledge of the general seasonal timing of cambial growth for a species and location. The presence of a fire scar on a tree implies that the fire that formed it was relatively low intensity and nonlethal, at least at the scale of the individual tree. By compiling dates of fire scars from multiple trees or plots across a landscape, the relative sizes and severities of past fires can be estimated with a great deal of accuracy (Farris et al. 2010). Increasingly, fire history studies use both tree age structure and fire-scar data to develop more complete estimates of the frequency and patterns of lethal and nonlethal burning across a study area (Brown et al. 2008). Furthermore, the accuracy of annual fire dates provided through dendrochronological cross-dating permits comparison of fire timing between sites, mountain ranges, and regions and with independently derived tree-ring reconstructions of climate variables (Swetnam and Brown 2010).

Important insights into historical fire climatology have been made owing to the accuracy of fire dates provided through regional networks of fire-scar records (Falk et al. 2011).

Other evidence of fires recorded by trees includes tree death dates and tree growth responses. Trees killed by fire can be dated by cross-dating with living trees. However, sapwood typically does not last very long after a tree is dead (even on standing dead trees, sapwood lasts at most a few decades; Fig. 1 left), which limits the length of time that this line of evidence can be used to reconstruct fire-caused mortality. Growth responses include abrupt growth suppressions or releases. For example, a growth suppression may occur after a fire as a result of severe scorching of a tree canopy. A growth release may occur as a result of neighboring trees being killed with a subsequent loss of competitive pressure on the surviving tree. Other responses include traumatic resin ducts or other ring features that indicate injury to the tree (Brown and Swetnam 1994).

A note of caution is warranted here, in that many other environmental factors may leave similar evidence in trees as those resulting from the effects of fire. For example, lightning and other injury events may partially kill the cambium and leave a scar in the ring series. The approach used by most studies has been to composite potential fire evidence from multiple trees in a stand or study area and depend on synchronous patterns as indications of fire timing and effects. For example, lightning will result in a scar on only a single tree in any given year, whereas fire scars will be recorded on several trees in the same year due to the spreading nature of fire within a stand of trees. Conversely, not all fires that burn at the base of a tree will leave a fire scar or other fire-caused evidence, and again compositing evidence from multiple trees is a usual step to compile more complete spatio-temporal fire histories (e.g., Farris et al. 2010). Dendrochronological cross-dating is, of course, crucial in these studies to provide absolute calendrical dates for fire evidence to assess synchronous or asynchronous patterns within and between trees, sites, or regions.

Application of Dendrochronological Fire Regime Studies

Studies using pyrodendroecological data have generally had three broad and often overlapping goals: (1) to document and characterize past fire effects on ecosystem processes, structure, and function across spatiotemporal scales; (2) to understand how fire regimes have been affected by forcing factors such as temporal or spatial changes in climate, human land use, and vegetation (fuel) structure; and (3) to develop historical information used in forest and ecosystem management. Pyrodendroecological data provide understanding of fire as an ecological process over periods longer than those available from typical ecological studies or even instrumental or observational records. For example, a major focus of many pyrodendroecological studies has been to examine longer-term (multi-decadal to multi-centennial) variation in fire climatology (Swetnam and Brown 2010; Falk et al. 2011). Fire history and other dendroecological data also provide “historical ranges of variability” in disturbance regimes and forest structure for ecological restoration efforts intended to restore ecological processes in degraded, damaged, or mismanaged forested ecosystems (Brown et al. 2008). This is especially the case in western North America where fire suppression efforts over the past century have led to profound changes in forest and fuel structure and fire regimes in many “fire-adapted” dry conifer ecosystems (e.g., Friederici 2003).

Conclusion

Dendrochronological methods are useful for dating, reconstructing, and interpreting past fires, fire regimes, and fire effects on individuals, communities, and ecosystems. Multiple lines of evidence of fire and its effects are recorded in tree-ring series, and many of these can be dated to the exact year and even season of formation. Pyrodendroecological data are useful not only for dating of fires but, more importantly, for understanding the role of fire in ecosystem structure and function; for understanding the role of climate, human land use, and vegetation structure on variations in fire regimes; and for current and future management of ecosystems around the world.

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Index Fossil

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Synonyms

[Guide fossils](#); [Range fossils](#); [Zone fossils](#)

Definition

A primary goal of the Earth sciences is to obtain as highly resolved correlations between different regions as possible. One of the most useful tools in this pursuit is the numerous fossils contained in most sedimentary units. The concept of using index fossils was initiated by the work of William Smith in the early 1800s; he used the fossil content of the units he examined as a critical component in the development of the first geologic map of the United Kingdom (Smith 1815). His observations on the distribution of fossils through time was formalized in his principle (or law) of faunal succession and served as the basis for determining the relative age of the rocks containing specific fossils. Building on Smith's concept, later workers used the temporal intervals defined by index fossils to represent range zones that form the basis of biostratigraphy, the science of correlation using fossils. Thus, index fossils form among the best components used in establishing a relative chronology and using that chronology to correlate globally.

Because all organisms evolve, this affords the opportunity to subdivide geologic time into a series of intervals characterized by individual, morphologically distinct species (the so-called morphospecies) into three intervals: an interval prior to their origination, one equivalent to their total temporal range, and another interval subsequent to their extinction. Therefore, any fossil species has the potential to be an index fossil. The best index fossils, however, tend to have the following characteristics: (1) rapid evolution so that the temporal intervals represented are short; (2) wide geographic distribution allowing correlation over a broad area; (3) virtually instantaneous range expansion following origination and simultaneous extinction decreasing the likelihood that these boundaries are time transgressive; (4) distinctive morphologic characters allowing differentiation from related taxa; (5) mineralized skeletal elements that are preserved in the fossil record; and (6) sufficient abundance affording the likelihood of finding their remains. Few taxa display all these characteristics, but that does not preclude their biostratigraphic utility.

Throughout the Phanerozoic, a broad range of different organisms has been used as index fossils. Given the criteria outlined above, the marine organisms that have proven most effective for defining short intervals are generally those that had planktic or nektic life habits. These floating/free-swimming organisms include both microinvertebrates (e.g., planktic foraminifers, radiolarians, and coccolithophores) and macroinvertebrates (e.g., ammonoids, graptolites). However, given the importance of determining the relative age of sedimentary units, representatives of

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virtually all phyla with a fossil record have been used including bivalves, brachiopods, corals, echinoids, gastropods, and trilobites (see Kauffman and Hazel (1977) for a more detailed treatment). Within the terrestrial realm, biostratigraphy has largely been based on pollen and spores as well as mammals (the so-called land mammal ages).

Cross-References

► [Geological Time Scale](#)

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Quartz

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On the Earth's surface, quartz (or, more properly, alpha-quartz) is by far the most common of the crystalline forms of silicon dioxide (SiO_2), constituting 12 % of the crust by volume. Among the igneous rocks, quartz is abundant within granites, granodiorites, pegmatites, and rhyolites. The weathering and erosion of these rocks tend to concentrate quartz as sedimentary particles because of its low solubility (~10 ppm) and its mechanical durability (with a Mohs hardness of 7 out of 10). As a result, quartz is the major constituent of highly mature arenitic sandstones. Quartz also can form in sedimentary environments through the chemical precipitation of dissolved silica. The dissolution of volcanic clays or of organosiliceous tests (as are found in diatoms, radiolaria, and sponges) produces a hydrous silica gel that will transform to quartz over thousands of years through diagenetic dehydration at temperatures up to 300 °C and pressures up to 2 kb. Metamorphism of siliceous sedimentary and igneous rocks will also induce quartz crystallization, and quartz is especially abundant within quartzites, schists, and gneisses. Additionally, hydrothermal alteration and fracturing of rocks may yield massive veins of quartz.

Quartz is differentiated from other silica minerals by its crystal structure and its field of thermodynamic stability. The low-temperature variety of quartz, called alpha-quartz (or low quartz), is stable when heated up to 573 °C and when stressed to pressures of 20–30 kb. When heated at atmospheric pressure above 573 °C, quartz transforms first to a structural variant called beta-quartz (or high quartz). On further heating, beta-quartz transitions to tridymite and thence to cristobalite before melting to silica liquid at 1,727 °C. When quartz at room temperature is pressurized to ~20 kb, it transforms to coesite; above 75 kb stishovite is the stable silica phase.

Euhedral crystals of quartz appear as hexagonal prisms capped at either or both ends by hexagonal pyramids, consistent with the underlying trigonal symmetry of alpha-quartz. The atomic framework of alpha-quartz consists of Si^{4+} cations that are tetrahedrally coordinated by oxygen anions (O^{2-}). Every oxygen anion is bonded to two silicon cations, so that the tetrahedral units are corner-linked to form continuous chains. In alpha-quartz, two distinct tetrahedral chains spiral about the crystallographic *c*-axis, creating ditrigonal tunnels along this direction (Fig. 1).

Although the tight crystal structure of quartz is not amenable to substitution by such radionuclides as U or Th, the past half century has seen major progress in the use of quartz for dating materials through luminescence-based approaches. Despite its apparent chemical simplicity, natural quartz crystals host a wide variety of defects, including vacant oxygen and silicon sites, as well as substitutional and interstitial cations (particularly H, Li, Al, and Fe). When quartz crystals are exposed to ionizing radiation (alpha, beta, gamma, or cosmic), these defects can serve as traps for free electrons generated by the radiation. Irradiated quartz crystals will luminesce when an external stimulation, such as from heat or light or stress, is applied, and the electrons are evicted from their traps to recombine with an appropriate defect center. In the absence of sunlight, some electron traps in quartz are thought to persist for hundreds of thousands to perhaps millions or

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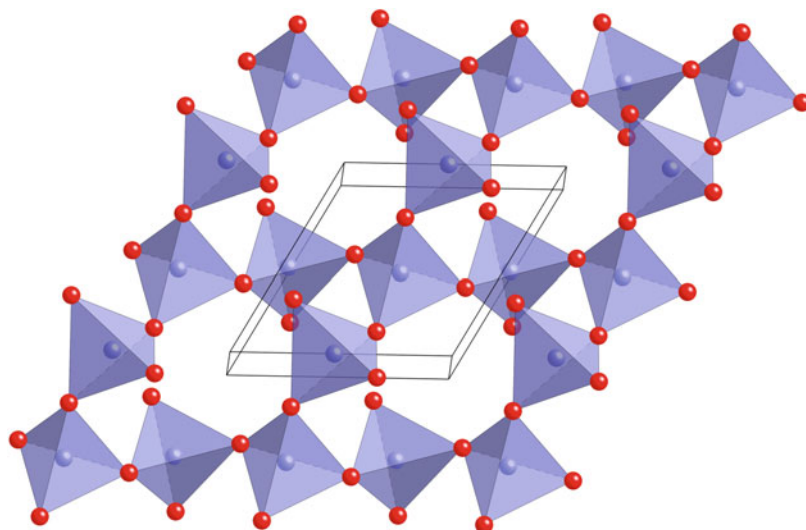


Fig. 1 Projection of the crystal structure of alpha-quartz along the crystallographic *c*-axis. Silicon atoms are *violet balls* and oxygen atoms are *red balls*

billions of years. The concentration of trapped electrons (and hence the intensity of the stimulated luminescence) increases with higher radiation dose until saturation is reached.

Through laboratory-based determinations of the relationship between radiation dose and light response, quartz crystals have been used to date geologic materials that were removed from sunlight and subsequently exposed to constant doses of ionizing radiation. Quartz-based luminescence has proven particularly successful in the chronometry of Quaternary sediments deposited by wind, water, and ice, but scientists have employed the technique for soils, volcanic rocks, and archaeological materials as well. Although many different luminescent stimuli have been experimentally investigated, heat and light are most commonly applied. Thermoluminescent (TL) dating involves heating quartz crystals at 5–20 °C/s and monitoring the temperature, wavelength, and intensity of the light emission. Most electron traps are emptied when quartz is heated above 500 °C, and emission events at 110 °C, 230 °C, 270 °C, 325 °C, and 375 °C are frequently observed. Scientists have attempted to relate these characteristic emissions to particular electron recombination centers. Optically stimulated luminescence (OSL) requires stimulation by light, typically using a laser emission in the blue-green portion of the electromagnetic spectrum, and the OSL emission occurs in the ultraviolet.

Recent studies have increased the sophistication of luminescence dating by combining these approaches (e.g., thermally transferred optically stimulated luminescence, or TT-OSL) and by analyses of multiple aliquots of a given sample. In addition to improving precision and accuracy, scientists hope that these approaches will extend the reach of quartz luminescence dating to a few million years.

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Molecular Clocks, Human Evolution

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Definition

Human evolution (molecular clocks). The timescale of human evolution and migration can be estimated from genetic data that have been sampled from living, historical, and ancient humans. This can be done using statistical methods based on the molecular clock hypothesis.

Introduction

The timescale of human evolutionary origins and migration across the globe has been a long-standing focus of scientific research. Genetic studies of the human evolutionary timescale were first performed in the 1960s, with the divergence time between humans and chimpanzees being estimated using data from the albumin protein (Sarich and Wilson 1967). The complete sequence of the human mitochondrial genome, consisting of about 16.5 thousand nucleotides, was published in 1981 (Anderson et al. 1981). Two decades later, the International Human Genome Consortium (2001) released a complete draft sequence of the much larger nuclear genome, comprising 3.2 billion nucleotides. DNA sequences of mitochondrial and nuclear genomes have now been obtained from a range of individuals throughout the world. The availability of genetic data from ancient samples has also been growing steadily (see “[Timescale of Human Evolution and Migration](#)” below).

Evolutionary timescales can be estimated from DNA sequence data using methods based on the molecular clock. The molecular clock hypothesis states that the rate of molecular evolution is constant among lineages (Zuckerkandl and Pauling 1962, 1965). If this assumption holds, then the difference between the DNA sequences of two individuals is proportional to the time since they last shared a common ancestor. If not, then there are various statistical methods that can account for rate variation among lineages and along the genome (Welch and Bromham 2005).

Until recently, genetic analyses of human prehistory were primarily based on mitochondrial DNA. The mitochondrial genome evolves rapidly and displays useful variation even over the short timescales associated with the prehistory of modern humans (Torroni et al. 2006). Substantial developments in DNA sequencing technology are enabling a growing focus on the nuclear genome, greatly increasing the data available for analysis. In addition, improving molecular techniques have made it possible to deal with contamination in ancient hominin samples. This has created opportunities to access genomic data from ancient modern humans, together with extinct species of hominins such as Neanderthals (Shapiro and Hofreiter 2010). These new sources of data have led to some significant changes to our understanding of hominin evolution. For example, DNA sequences of ancient genomes have shed light on interbreeding between Neanderthals and modern humans

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(Prüfer et al. 2014), our relationships with ancient hominins (Reich et al. 2010), and the timescale and patterns of human dispersals across the globe (Reich et al. 2011).

The Human Molecular Clock

For several decades, the mitochondrial genome was the dominant source of information for estimating molecular rates of evolution in humans and other hominins. In analyses of human mitochondrial genomes, a common approach is to employ an estimate of the evolutionary rate from a previous study, with a small number of “standard” rates dominating the literature (Endicott et al. 2009). Most of these rates were estimated by assuming that humans and chimpanzees diverged from each other about 6.5 million years ago, based on fossil evidence.

Pedigree studies, which involve the analysis of DNA sequences from multiple members of a family, have yielded very high estimates of mitochondrial mutation rates (Howell et al. 2003). There is a substantial discrepancy between these estimates and those based on comparisons between humans and chimpanzees. This pattern can be explained by a number of biological and statistical factors (Ho et al. 2011), including the effects of natural selection. The presence of transient deleterious mutations at the pedigree level, which are removed over time by negative selection, causes an apparent short-term elevation of evolutionary rates (Soares et al. 2009).

In analyses of mitochondrial genomes, the evolutionary rate is typically assumed to be constant among lineages. However, there is considerable evidence for rate variation among species and even among human populations (Henn et al. 2009). In addition, there are limits to the interpretation of analyses based on mitochondrial DNA, owing to the fact that it is only a single genetic marker (Balloux 2010). This is in contrast with the nuclear genome, which contains thousands of independent markers that can be used to trace evolutionary patterns and timescales.

In the post-genomic era, sequences from the nuclear genome have become readily available. This important source of data has provided a broad range of insights into human evolution. A prominent feature of genomic evolution in primates is a decline in evolutionary rates within hominoids compared with their relatives (Goodman 1985; Steiper et al. 2004). The hominoid slowdown can be partly explained by differences in generation times. In species with longer generations, the genome experiences fewer replications per unit of time. During replication, copying errors lead to mutations in the genome, and these can be inherited by descendants.

More recently, studies at the pedigree level have yielded estimates of the *de novo* mutation rate in the human nuclear genome. These have produced an unexpected result, with the *de novo* mutation rate being about half of the rate estimated using a human-chimpanzee comparison (e.g., Roach et al., 2010). A possible explanation for this pattern is that humans have longer generation times than chimpanzees, which would lead to a lower rate of evolution. This lower rate has the effect of increasing date estimates for key phases in human prehistory, such as the most recent common ancestor in Africa (Sally and Durbin 2012). The archaeological evidence for detecting population-level events in human evolution is rather scant, and it is not yet clear whether such revised dates are supported.

Timescale of Human Evolution and Migration

Estimates of the human evolutionary timescale have varied considerably, depending on the choice of genomic marker, the breadth and depth of sampling, the calibrations used for the molecular

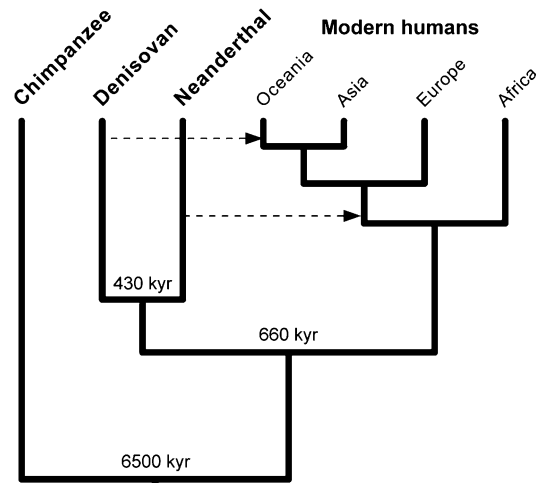


Fig. 1 Phylogenetic tree showing the evolutionary timescale of modern humans, Neanderthal, Denisovan, and chimpanzee. *Dashed lines* indicate genetic contributions made from Neanderthals and Denisovans to populations of modern humans. Date estimates are from Prüfer et al. (2014). The tree is not drawn to scale

clock, and the method of analysis. In some cases, different date estimates support conflicting interpretations of human evolution and prehistory.

Studies of mitochondrial DNA have yielded date estimates that have been broadly consistent with the timescales inferred using archaeological and paleontological approaches. The lineage leading to modern humans diverged from Neanderthals about 400,000 years ago (Endicott et al. 2010). Living modern humans share a common mitochondrial ancestor, sometimes referred to as “mitochondrial Eve,” who lived in Africa over 100,000 years ago. Humans then migrated to Eurasia and Australasia about 50,000–60,000 years ago, reaching the Americas about 15,000 years ago.

DNA sequences from ancient specimens have had a major impact on our understanding of human prehistory. Significant advances in molecular technology have enabled entire mitochondrial and nuclear genomes to be sequenced from samples that are tens to hundreds of thousands of years old, provided that they have been preserved under certain conditions. Estimates from the nuclear genome indicate that modern humans and Neanderthals diverged more than 600,000 years ago (Fig. 1; Prüfer et al. 2014), although estimates range from 400,000 to 800,000 years. Neanderthals and another group of hominins known as Denisovans split from each other about 430,000 years ago. After this event, Neanderthals contributed genetic material to non-African modern humans, whereas significant amounts of Denisovan DNA appear only in modern humans from Oceania (Fig. 1).

Future Directions

Our understanding of the timescale of hominid and human evolution is constantly being refined. The genomic era has brought a wealth of data, offering the possibility of resolving human prehistory at an unprecedented level of detail and precision. The data being produced can yield large numbers of neutral markers for use in large-scale analyses. Additional benefits will come from further sampling of global genetic diversity, particularly in regions that are poorly represented. Genetic estimates of the human evolutionary timescale will continue to improve

with progress in identifying reliable calibrations for the human molecular clock, such as dates based on Paleolithic archaeology or biogeography. Genomic analysis of ancient human specimens represents a particularly promising area of research and has the potential to transform our understanding of the evolutionary origins of our species.

Cross-References

- ▶ [Gene Sequencing](#)
- ▶ [Molecular Clocks](#)
- ▶ [Molecular Clock Calibrations](#)
- ▶ [Molecular Clocks, Relaxed Variant](#)
- ▶ [Molecular Dating of Evolutionary Events](#)
- ▶ [Molecular Rate Variation \(Molecular Clocks\)](#)
- ▶ [Polymerase Chain Reaction DNA Amplification](#)

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Molecular Clock Calibration

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Synonyms

[Calibration prior](#); [Fossil calibration](#); [Molecular clock constraint](#); [Time prior](#)

Definition

Molecular clock calibration. The temporal information used to calibrate the molecular clock and estimate the molecular substitution rate.

The Molecular Clock

Establishing an evolutionary timeline for the tree of life (TOL) is essential for understanding the history of biodiversity. The incompleteness of the rock and fossil record means this cannot be achieved using paleontological evidence alone. The molecular clock provides the only viable means of obtaining precise estimates of evolutionary time. The mutations that arise along a gene sequence represent copy errors that accumulate randomly over time. The differences observed between the genes of two living species are therefore a function of the time since they last shared a common ancestor. If the age of the last common ancestor can be determined from the fossil record for a pair of living species, the clock can be *calibrated* and the rate at which mutations have accumulated can be calculated. The molecular clock can then be used to infer the time of divergence of other species pairs. In practice, different branches of the TOL accumulate genetic changes at different rates, and precise calibrations cannot be obtained from the fossil record. Over the past 50 years, molecular clock methods have evolved to become increasingly sophisticated. Relaxed clock models can be used to accommodate rate variation, the process of molecular evolution can now be modeled more realistically, and these methods continue to be developed (Sanderson 1997, 2002; Thorne et al. 1998; Drummond et al. 2006; Rannala and Yang 2007; Drummond and Suchard 2010). There have been parallel developments in the way in which the clock is calibrated (Sanderson 1997; Thorne et al. 1998; Drummond et al. 2006; Yang and Rannala 2006; Inoue et al. 2010). Deriving paleontologically based calibrations, and quantifying the associated uncertainty, requires a careful evaluation of the way in which temporal information can be extrapolated from the fossil record (Reisz and Müller 2004; Benton and Donoghue 2007; Donoghue and Benton 2007; Parham et al. 2012).

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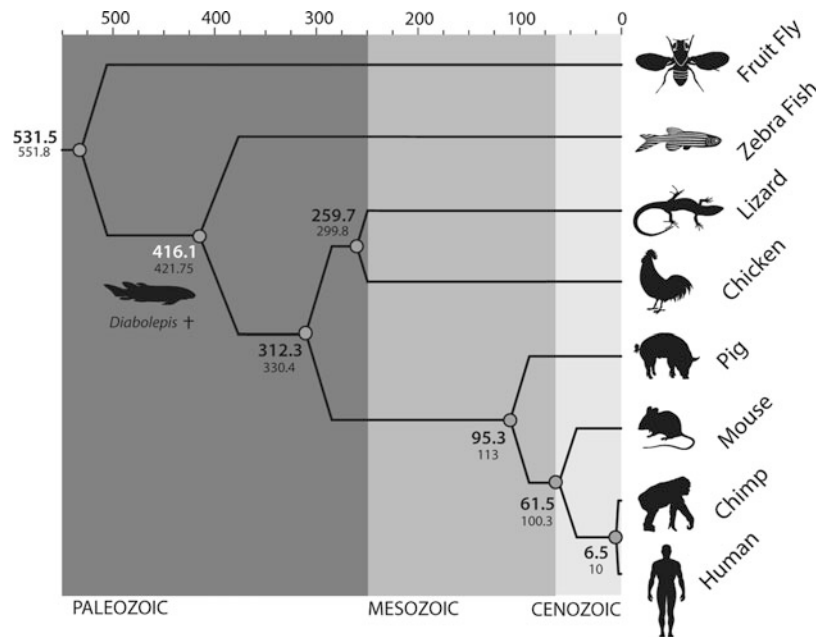


Fig. 1 Tree illustrating the minimum and maximum divergence times among several model animal species based on fossil evidence. As an example, the divergence event between human (Actinopterygii) and zebra fish (Sarcopterygii) is highlighted. The minimum constraint (*highlighted in white*) is represented by one of the earliest known sarcopterygians, the lungfish *Diabolepis*. Minimum constraints for all divergence events are shown in **bold**; maximum dates are shown below. These examples are taken from Benton and Donoghue (2007)

Uncertainty in the Fossil Record

The fossil record is incomplete. Only a tiny fraction of all life that has ever lived has been preserved in the rock record, and some branches of the TOL are entirely absent (Raup 1972). However, the process of preservation and discovery is far from random, and the quality of the fossil record is immensely variable over geological time. There are many variables which predicate the probability that an organism will ever be preserved in the fossil record, and further obstacles that determine the probability that it will later be sampled and identified correctly by paleontologists.

Fossils are the remains of once living organisms that have been mineralized and preserved in the rock record. Different anatomical and skeletal features have variable fossilization potential, contingent on their chemical structure and the environment in which they degrade and become deposited. An organism's physiology, habitat preferences, and life history all contribute to the likelihood of preservation, and the probability of becoming fossilized can alter over time, for example, by the acquisition or loss of hard parts.

The rock record, in which the fossil record is embedded, is also spatially and temporally biased (Smith 2007), and there exists a strong, unresolved correlation between the two (Smith and McGowan 2007; Peters 2005; Benton et al. 2011). To some extent the fossil record must be subject to the artifacts of the rock record, because the appearance of an organism in the fossil record is contingent on the availability of rock units suitable for preservation and subsequent sampling (Peters and Foote 2001). Widespread heterogeneity in the deposition of sediments means the fossil record is heterogeneous both temporally and regionally. Older rocks are also more likely to have been eroded or altered by temperature and pressure. The way paleontologists sample the rock record is also influenced by the exposure and access to fossil-bearing rocks, and variable interest in different groups of fauna and formations (Dunhill 2012).

Most importantly for telling evolutionary time, the first appearance of a species in the fossil record is not coincident with the time of origin, because the probability of sampling the earliest member of a lineage is virtually zero and because it will be indistinguishable from its direct ancestor. The large number of variables that contribute to the probability that an organism will be preserved and later sampled creates huge variability in the extent of the gaps in the fossil record across the TOL. This means different fossils approximate divergence times to different degrees. Understanding the incompleteness of the fossil record forms an active and important branch of paleontology. It is important to recognize the factors that both prohibit and facilitate the process of fossilization as part of any attempt to extrapolate information from the fossil record. How we calibrate the molecular clock from such an incomplete record is not obvious.

Minimum and Maximum Constraints

The fossil record can never provide a precise time of origin for any species, but this is not equivalent to saying that the fossil record cannot provide accurate estimates. The order in which organisms first appear in the fossil record is roughly congruent with the order in which the branches of the TOL diverged genetically, meaning that the fossil record captures reality on some level (Benton et al. 2000). Using a critical approach, paleontological evidence can instead be used to constrain divergence events by providing minimum (or maximum) ages that can be incorporated into the calibration of the molecular clock (Fig. 1). First appearances provide an obvious source for defining minimum constraints, because they must postdate the time of origin of all evolutionary lineages.

An individual fossil specimen can never provide more than a minimum point of divergence, but maximum constraints are also essential for calibrating the molecular clock (Sanderson 1997; Kishino et al. 2001; Thorne and Kishino 2005; Yang and Rannala 2006). The maximum has to define the point before which evidence suggests the divergence event has not yet occurred. How far back beyond the minimum constraint is the evolutionary history of a clade likely to extend? The variable length of gaps in the fossil record makes this extremely difficult to estimate.

Maximum constraints can be established by taking into account a wider suite of paleontological evidence. One strategy is to use the fossil record of closely related evolutionary branches (phylogenetic bracketing) (Reisz and Müller 2004; Müller and Reisz 2005). The first appearance of the descendants of the proceeding divergence event may be useful for defining the maximum. This requires an assessment of the quality of the records on either side of the divergence event, because this approach relies on the assumption that there is perfect congruence between the order of branching events and the sequence in which lineages first appear in the fossil record. We know that this assumption will be violated for some species due to nonrandom preservation. An alternative, more conservative approach can be adopted to define the maximum, by tracing the record back to a time period during which conditions conducive to preservation are met, but nothing resembling the group of interest has ever been discovered, taking into account a species' ecology, biogeography, preservation potential, and sampling (Benton and Donoghue 2007; Parham et al. 2012).

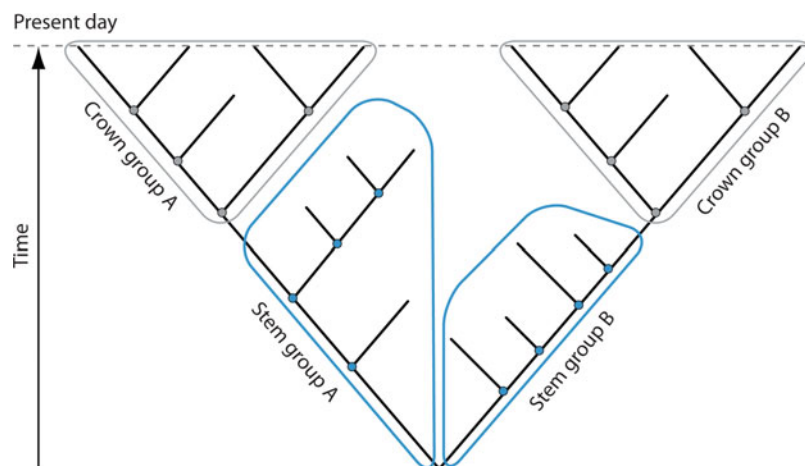


Fig. 2 Definitions of crown and stem groups. The crown group (*shaded in grey*) represents all living members of a group, along with their common ancestor, and all extinct relatives in between. The stem group (*blue*) represents all the extinct members of a group that are more closely related to their crown group than to any other

The Relationship Between Fossils and Living Species

For a fossil to be useful for defining the minimum constraint of a divergence event, it must be certain that the fossil belongs to one of the descendant branches (the crown group), and not to some extinct ancestral branch that predates the point of divergence (the stem group) (Fig. 2). Understanding the evolutionary – or phylogenetic – relationships among living species is greatly facilitated by molecular sequence data; however, for organisms known only from the fossil record, relationships can only be inferred from morphological characters. This can be difficult because many extinct species are known only from very fragmentary fossil remains, or come from rocks, which have been highly eroded over time. The earliest members of a group will also be the most difficult to distinguish from the ancestral members, and in some cases the most distinguishing features of a group may be among the first to be degraded prior to fossilization (Donoghue and Purnell 2009; Sansom et al. 2010). There can also be a dramatic conflict between the relationships suggested by independent pools of phylogenetic evidence (e.g., molecular versus morphological data). If the relationship between a fossil specimen and other species (relative to the divergence event) cannot be established, that specimen cannot be used reliably to inform the minimum constraint. It is necessary to examine as much evidence as possible and use robust tree building programs to establish the relationships among fossils and living species.

Establishing the Absolute Age of a Calibration

We need to know the age of the source rock yielding the fossil specimens used to inform calibrations. It is rarely possible to derive the age directly from the specimens, so the age of the locality from where the fossil was sampled must be established. Firstly, accurate locality information must be obtained. This information varies in precision among specimens; some records will refer to a well-constrained level in a stratigraphic section, while others only indicate the relevant geological formation or group. Secondly, the age of the locality must be established. If the locality has not been directly dated (absolute dating), or the available radiometric date is not stratigraphically relevant for defining the minimum or maximum age limits, it will usually be necessary to

establish the age through stratigraphic correlation (relative dating). Once the age of the source rock is known relative to the geological timescale, the absolute age can be defined with reference to the international chronostratigraphic chart. A conservative interpretation is necessary to maintain accuracy. Minimum (or maximum) constraints should be based on the youngest (or oldest) possible interpretation of the fossil specimen. The age should correspond to the explicitly defined top (or base) of a geological time period and should include the associated radiometric dating error (Benton and Donoghue 2007; Parham et al 2012).

Tectonic Calibrations

Tectonic calibrations provide an alternative to fossil calibrations, based on the tectonic events that lead to the initial separation of two evolutionary lineages, such as the fragmentation of supercontinents, the opening of oceans, or the formation of volcanic islands. The tectonic movements that were the key to stimulating divergence among species may be manifested in the modern biogeographic ranges of the independent lineages. The use of tectonic calibrations circumvents many of the problems associated with fossil-based constraints, such as the necessity to define evolutionary relationships among extinct and living species *a priori*. But like fossil-based calibrations, the uncertainty associated with the age of tectonic events must be established, and in some cases this uncertainty can be extremely large.

Firstly, it must be established whether a given tectonic event was actually causal to the speciation event (Kodandaramaiah 2011). This requires establishing whether the modern species ranges reflect the ancestral biogeography. Tectonic events will also have variable impacts on the ecology and biogeography of different species (Goswami and Upchurch 2010). For example, an oceanic barrier might limit the dispersal of a freshwater amphibian species, but will not pose the same limitations for some bird species. The precise point at which a tectonic event becomes a complete dispersal barrier will be hard to define. Secondly, the age of the event must be established. Many tectonic events can be protracted over long episodes (e.g., tens of millions of years), and it can be difficult to pinpoint rock sources that constrain the temporal episode. The dating errors associated with the rock ages must also be considered, as above.

For groups with a very sparse fossil record, tectonic calibrations provide an excellent source, independent from the fossil record, for establishing constraints (Bromham and Penny 2003). However, fossils (perhaps of other species) will remain integral for verifying the relationship of tectonic events on modern biogeography. Tectonic calibrations should be subject to the same scrutiny with which fossil calibrations are established (Goswami and Upchurch 2010), but similarly the associated uncertainty can be quantified and modeled in molecular clock analyses.

The Development of Different Approaches to Implementing Calibrations

Traditionally calibrations were implemented as fixed points (Zuckerandl and Pauling 1962), making an assumption that there was no uncertainty associated with the calibrations and that ages obtained from the fossil record were known perfectly. However, there is often a great deal of uncertainty associated with the calibrations. Computational progress has enabled molecular clock methods to become increasingly sophisticated. Maximum likelihood approaches allowed the implementation of minimum and maximum constraints that could reflect a range of calibration ages, instead of fixed points (Sanderson 1997, 2002). There has now been a shift into the Bayesian

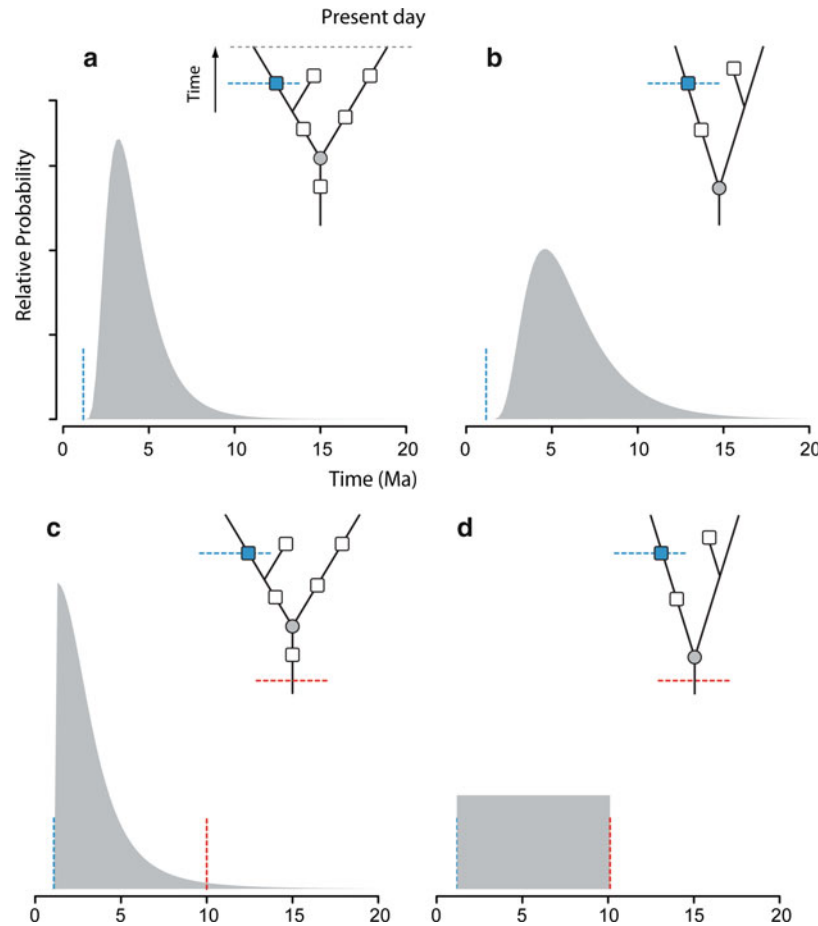


Fig. 3 Example calibration priors used in Bayesian molecular clock analyses. The *top panel* shows a hypothetical divergence event (*shaded in gray*) and fossil occurrences (*squares*). The oldest fossil that can be unambiguously assigned to the crown group and the minimum constraint are highlighted in *blue*. The maximum constraint is represented by the *dashed red line*. The *bottom panel* shows the prior probability functions. The y-axis represents the relative probability of divergence. In **a** and **b** the calibration prior is defined using the lognormal distribution based on the minimum constraint only (1 Ma) (**a**: $\mu = 1$; $\sigma = 0.5$; **b**: $\mu = 1.5$; $\sigma = 0.5$). **c** is an example using the skew-*t* distribution. The parameters were selected such that the 97.5 % interval matches the maximum constraint (10 Ma) ($\xi = 1$, $\omega = 2$, $\alpha = 100$, $\nu = 2.73$). **d** is an example using a uniform distribution between the minimum and maximum constraints

framework (Thorne et al. 1998; Drummond et al. 2006; Yang and Rannala 2006). The posterior probability for divergence times

$$Pr[Times | Sequence data] = Pr[Sequence data | Times] * Pr[Times] / Pr[Sequence Data]$$

combines the prior probability of divergence times ($Pr[Times]$) with the likelihood ($Pr[Sequence data | Times]$). The prior probability is used to express our prior knowledge of divergence times and contains the calibration information.

In the original Bayesian implementation, the calibrations could be implemented as minimum and maximum constraints (Thorne et al. 1998), but further development has led to increased flexibility. Each variable that describes the probability of divergence times can now be modeled independently, and all unknown parameters can be assigned an independent prior distribution

(Drummond and Rambaut 2007). The calibrations can be expressed using any of a huge variety of functions that best describe the relationship between the uncertainty inherent in the calibrations and the true divergence times (Yang and Rannala 2006; Drummond et al. 2006; Inoue et al. 2010) (Fig. 3). The uncertainty associated with all unknown parameters is considered in the estimation of evolutionary rates and times, and the output (the posterior probability) will be a distribution of values that reflects the underlying uncertainty in the estimates.

The Bayesian approach to estimating divergence times is appealing not only because it offers a great deal of flexibility, but it is also the only method that will allow the uncertainty associated with the calibrations to be reflected in the results (Thorne and Kishino 2005). Because this error can be large, this is extremely important. The way in which calibration uncertainty is represented in molecular clock analysis can have a pejorative impact on the results (Ho and Phillips 2009; Inoue et al. 2010; Clarke et al. 2011; Warnock et al. 2012). It is therefore imperative for the accurate estimation of rates and times that calibration uncertainty be accurately quantified and represented.

Characterizing the Shape of Uncertainty from the Fossil Record

Beyond establishing minimum and maximum constraints, perhaps the most challenging element of establishing molecular clock calibrations is characterizing the temporal relationship between the fossil evidence and time of origin. The function used to express the calibration prior has to reflect the probability of divergence relative to the first appearance in the fossil record. A huge variety of functions, such as the lognormal, exponential, and uniform (Fig. 3), have been integrated into Bayesian molecular clock software for this purpose. The distribution used for the calibration prior should depend on the available fossil evidence.

The minimum constraint represents the youngest possible time of divergence and can be used to define the lowest limits of the calibration prior. The peak in prior probability, representing the most likely time of divergence, occurs at some time before the first appearance in the fossil record, with a diminishing probability that divergence has occurred as you go further back in time. For an organism with a good, dense fossil record, the first appearance might provide a very good approximation of the true divergence time, so the peak in prior probability might occur close to the minimum constraint (Fig. 3a). Conversely, for a group with a very sparse record, the first appearance may provide a very poor approximation of the time of origin, and a more diffuse prior distribution might be more appropriate (Fig. 3b). In reality, it is extremely difficult to infer this relationship, and limited protocols exist for choosing the shape of the prior probability function and choosing the distribution parameters.

These parameters should not be chosen arbitrarily: a meaningful maximum constraint is also required for the estimation of the substitution rate (Sanderson 1997; Kishino et al. 2001; Thorne and Kishino 2005; Yang and Rannala 2006). A soft maximum constraint provides a useful guide for the selection of the distribution parameters, by defining the upper confidence limits of the distribution (e.g., the 95 % or 99 % limits) (Fig. 3c) (Ho and Phillips 2009; Warnock et al. 2012). However, this does not eliminate the requirement to specify the location of the peak in prior probability. In the absence of any alternative justification, a uniform distribution with an equal probability between the hard minimum and soft maximum constraints may provide the best characterization of the available evidence (Fig. 3d) (Benton and Donoghue 2007).

More comprehensive approaches are available for constructing probabilistic calibration priors based on additional phylogenetic and paleontological information. The most likely divergence time can be calculated based on the first occurrences of closely related species (Hedman 2010) or

modeled using total group fossil occurrence data (Strauss and Sadler 1989; Marshall 1997). The most complex models can incorporate estimates of speciation and extinction rates over time and nonrandom sampling of the fossil record (Foote et al. 1999; Tavaré et al. 2002; Wilkinson et al. 2010). These approaches present an excellent opportunity to integrate more paleontological evidence into the molecular estimation of divergence times, but the required comprehensive and well-curated fossil datasets are often unavailable.

Like any scientific variable based on independent sources of evidence, calibrations are dynamic values. The understanding of relationships among different branches of the TOL is continually updated, new fossil finds can update minimum or maximum constraints, and the geological timescale is perpetually refined and revised. Calibrations should be updated in light of evolving evidence.

The Inclusion of Extinct Species in the Estimation of Divergence Times

Phylogenetic tree building methods also enable the simultaneous estimation of evolutionary relationships and divergence times (Drummond et al. 2006; Ronquist et al. 2012a). However, the popular approach of incorporating calibrations in the form of prior constraints on divergence events necessitates that the relationships between the fossils and living species be known a priori. An alternative approach is to include the fossils of known age as branches in the phylogeny (Pyron 2011; Ronquist et al. 2012b). This allows the relationships of extinct and extant species, as well as the evolutionary times to be co-estimated (this is how viral trees are typically dated, using the molecular sequences of archived strains). Although molecular data can rarely be obtained from extinct or fossil specimens, morphological data can be obtained from fossils, and because living (or extant) organisms possess both sources of data, the information can be combined. The major advantage of this approach is that it eliminates the difficult quest of assigning a probability of divergence time relative to the paleontological evidence. However, this approach is accompanied by its own caveats. It requires the fossil record of the group to be relatively comprehensive, and appropriate morphological datasets are rarely available. The fragmented or eroded nature of many fossils, and the absence of any molecular data to accompany the morphological data for fossil specimens, introduces a large amount of missing data and additional uncertainty into the analysis. It also requires the assumption that a clock-like model of evolution can be applied to morphological data.

Current and Ongoing Controversies

Initially there were huge discrepancies between the evolutionary times implied by paleontological evidence and the times inferred from the molecular clock. This is partially because traditional molecular clock methods demanded the use of point (or fixed) calibrations. These were typically based on inaccurate interpretations of first appearances, and early molecular clock estimates for many groups hinted at much more ancient origins than those inferred from the fossil record alone. The timing of origin of the organisms present during and at the end of the Cambrian explosion is one notable example (which represents the first appearance of all the major animal phyla in the fossil record, around 541 Ma). Early molecular clock estimates suggested an age of more than twice that implicated by the fossil record for the origin of most animal phyla (Hedges and Kumar 2003).

The large deviations between the timescales obtained from the molecular data were initially used to denigrate the veracity of the fossil record as an accurate document of evolutionary history.

Parallel improvements in the way in which rate variation and calibration uncertainty can be modeled in molecular clock analyses have resulted in the reducing of the gap between molecular clock estimates and the fossil record. Recent estimates place the origins of the Cambrian animal fauna at 619–546 Ma (Rota-Stabelli et al. 2013). A degree of discrepancy is inevitable given the paucity of the fossil record, but the questions have now become more intellectual. How much of the fossil record can be anticipated to be missing? Could the morphology of the common ancestor of animals explain its absence from the record? A concrete collaboration between geologists and molecular biologists is essential, both for tackling these questions and for establishing a more precise timescale for the evolution of life.

In reality, we can never know the correct time of divergence relative to appearances in the fossil record, so we can never assess the accuracy of molecular clock estimates using empirical datasets. The solution is to use artificial, or simulated, datasets where the relationship between the fossil evidence and genetic divergence is known. Fossil occurrences can be simulated using a simple model of nonuniform preservation that describes the stratigraphic distribution of fossils observed in the fossil record (Holland 1995, 2000). Models of speciation, molecular sequence evolution, and fossil preservation can be combined in simulations to test different approaches to establishing calibrations and, ultimately, the performance of the molecular clock.

Summary

The incompleteness of the rock and fossil records means they cannot be used to establish a precise timeline for evolutionary history. The molecular clock provides a useful alternative, but the temporal calibrations required to estimate the substitution rate must be derived from paleontological evidence. The nonrandom nature of fossil preservation and recovery makes this extremely difficult. Although precise calibrations cannot be derived from the fossil record, they can instead be used to accurately define minimum and maximum constraints on divergence ages. The next challenge is to characterize the relationship between the constraints and divergence times. Approaches to do so have become increasingly complex and continue to progress to allow more information to be captured in the estimation of evolutionary times. Molecular estimates of times and rates will only ever be as accurate as the calibrations on which they are based, making it essential to embrace and understand the uncertainties inherent in the fossil record. Adopting a holistic approach through the integration of paleontological and biological expertise can make the molecular clock one of the most powerful tools in evolutionary biology.

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Radiation and Radioactivity

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Definition

Radiation: The term radiation includes the whole electromagnetic spectrum as well as all atomic and subatomic particles. Ionizing radiation refers to the ability of certain types of radiation to ionize the medium they traverse. Only ionizing radiation will be considered here.

Radioactivity: The spontaneous emission of particles or electromagnetic rays from unstable atomic nuclei.

Introduction

In 1895 Wilhelm Conrad Röntgen experimented with a Crooke's tube, an evacuated glass enclosure in which current can be passed through a high vacuum from one electrode to another. He noticed that a small screen placed at some distance started fluorescing when the tube was on. Röntgen named the unknown radiation X-rays. He observed that they could penetrate paper and wood, but would be absorbed by aluminum and tin foil. Encouraged by Röntgen's observations, Henri Becquerel experimented with uranium minerals which he placed on photographic plates. He found that the plates showed signs of exposure even in the absence of light and eventually named the uranium emissions α - and β -rays. In 1897 Marie and Pierre Curie made similar observations in experiments with other elements and suggested the term "radioactivity" to describe the phenomenon. Many further discoveries have led to an increased understanding of the atomic and nuclear structure and the processes leading to the emission of ionizing radiation. Today radiation and radioactivity have found application in fields as varied as medicine, energy production, and dating.

Structure of the Nucleus

Atoms consist of a positively charged nucleus around which negative electrons revolve in stable orbits, bound by electrostatic coulomb forces due to their opposite charges. The nuclei consist of positively charged protons and electrically neutral neutrons which are collectively referred to as nucleons. The atomic number, Z , is defined as the number of protons in a nucleus. The number of neutrons is designated by the neutron number, N . The mass number, A , is the total number of nucleons in a nucleus. An arbitrary element X with atomic number Z and mass number A is denoted by ${}_Z^AX$, e.g., carbon-14 with its 6 protons and 8 neutrons is written as ${}_6^{14}\text{C}$. All nuclei of a given element have the same number of protons, but may have different numbers of neutrons. Such nuclei are referred to as isotopes (e.g., ${}_6^{12}\text{C}$, ${}_6^{13}\text{C}$, ${}_6^{14}\text{C}$).

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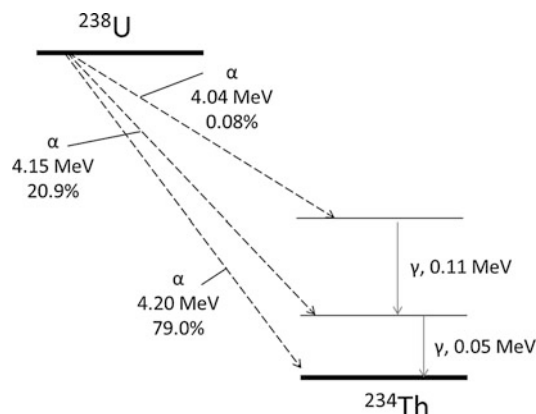


Fig. 1 α -Decay scheme of ^{238}U to ^{234}Th . After emission of the α -particle, ^{234}Th can be left in the ground state or one of the two excited states. Decay to an excited state is followed by de-excitation and emission of γ -rays. The scheme shows possible α -energies and their emission probabilities in percent, as well as possible γ -energies (Data from Table of Nuclides, Korea Atomic Energy Research Institute)

The positive protons in the nucleus repel one another. However, the nucleus is held together as a result of the strong nuclear force. Nuclei can only exist at certain discrete energy states, similar to the energy states of the atoms themselves. The distance between these nuclear energy levels is on the order of keV or MeV while atomic levels are on the order of eV. The number of levels increases with the mass number, A . The lowest energy state is called ground level. If the nucleus is excited above this level, it can de-excite by emitting a photon and/or one or several nucleons.

The stability of a nucleus depends on its number of protons and neutrons. Nuclei of relatively small atomic numbers are most stable when the numbers of protons and neutrons are comparable. $^{12}_6\text{C}$ and $^{13}_6\text{C}$ are both stable. Heavy stable nuclei contain considerably more neutrons than protons, such as the stable bismuth isotope $^{209}_{83}\text{Bi}$, which contains 83 protons and 126 neutrons. Bismuth is the heaviest element with a stable isotope. For nuclei with $Z > 83$ the strong nuclear force can no longer compensate the repulsive forces between the protons and the nuclei disintegrate by a process of decay.

Radioactivity

Unstable nuclei emit particles until they reach a stable composition, and until stable they are “radioactive.” This process is often accompanied by a rearrangement of the nucleons within the nucleus to a lower-energy state, which leads to the emission of a high-energy photon – comparable to the emission of photons during the de-excitation of electrons. The most important decay modes are α -, β -, γ -decay, and fission.

α -decay is predominantly observed for heavier nuclei with $Z > 83$. The nucleus decays by emitting an α -particle, ^4_2He , in which process it loses two protons and two neutrons:



X is referred to as parent nuclide and Y is the daughter nuclide. For example, the parent $^{238}_{92}\text{U}$ decays to its daughter $^{234}_{90}\text{Th}$ by emitting an α -particle. The decay often leaves the daughter nuclide in one of several possible excited states, where each state is reached with different probability (see

Fig. 1). α -Particles can therefore be emitted at several discrete energies characteristic to the parent nuclide.

In **β -decay** a nucleus emits an electron or positron. β^- -decay is the conversion of a neutron to a proton, under the emission of an electron and an electron antineutrino:



It is observed for nuclides with an excess of neutrons and the process can be described by



A prominent example is the decay of radiocarbon to nitrogen: ${}_6^{14}C \rightarrow {}_7^{14}N + e^- + \bar{\nu}_e$.

β^+ -decay refers to the conversion of a proton to a neutron, under emission of a positron (i.e., the positively charged antiparticle of the electron) and an electron neutrino:



An example is the decay of ${}_{12}^{23}\text{Mg}$ to ${}_{11}^{23}\text{Na}$. Similar to α -decay, the daughter nuclide is often left in one of several possible excited states. Unlike α -particles, however, electrons and positrons do not have discrete energies. β -decay results in two particles and the energy can be divided between the particles in an infinite number of ways. Therefore β -particles are emitted with continuous energies; the spectrum is a curve with a maximum at intermediate energies and extends to an energy maximum.

α - and β -decays often leave the parent nucleus in an excited state, similar to an excited atom. The nucleus reaches a lower-energy state by rearranging the protons and neutrons and by emitting a high-energy photon, a γ -ray (compare Fig. 1). The discrete energies of these γ -rays are characteristic for the parent nuclide and are in the keV-MeV range. Neither atomic number nor mass number is changed during **γ -decay** of a nucleus.

Spontaneous **fission** is only observed for high mass numbers. In the process the nucleus splits into two smaller nuclei. Several neutrons and large amounts of energy are released during this process. For ${}^{238}\text{U}$ the probability to decay via α -decay is 10^6 times larger than the probability to undergo spontaneous fission, but this process varies among nuclides. In some nuclei such as ${}^{235}\text{U}$, fission can be induced by absorption of a slow neutron, resulting in an excited ${}^{236}\text{U}$ nucleus, which ultimately splits into two smaller nuclei.

Activity and Half-Life

Activity, A , is the rate at which unstable nuclei decay, i.e., the number of decays per second. Two units are commonly used for activity:

$$1 \text{ curie} = 1 \text{ Ci} = 3.7 \times 10^{10} \text{ decays/s}$$

which is the activity of 1 g of radium and the SI unit

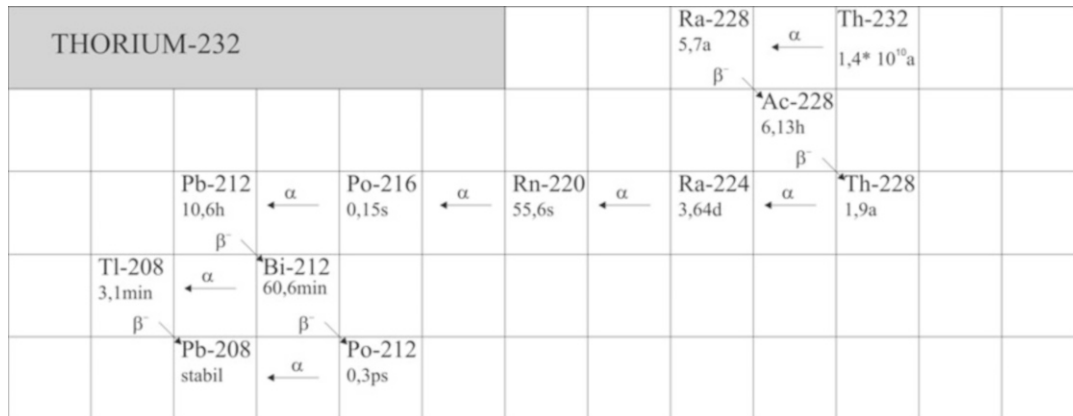


Fig. 2 Thorium decay series. The nuclides, their type of decay (α or β), and their half-lives are indicated

$$1 \text{ becquerel} = 1 \text{ Bq} = 1 \text{ decay/s.}$$

The conversion factor is $1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$.

The number of unstable parent nuclei decreases exponentially over time. Given an initial number N_0 of parent nuclei at start time $t = 0$, the number N of nuclei remaining at time t is given by

$$N = N_0 e^{-\lambda t} \quad (6)$$

λ is referred to as the decay constant with unit s^{-1} . The larger the decay constant, the more rapidly the number of parent nuclei decreases with time. The decay constant is characteristic for each radioactive nuclide. The activity depends on the number N of nuclei and the decay constant:

$$A = \lambda N \quad (7)$$

Related to the decay constant is the half-life $t_{1/2}$ of a radioactive nucleus:

$$t_{1/2} = \frac{\ln 2}{\lambda} \quad (8)$$

The half-life is the time in which the number of parent nuclides decreases by a factor 2, i.e., from N_0 to $\frac{1}{2}N_0$ and from $\frac{1}{2}N_0$ to $\frac{1}{4}N_0$.

By determining the current number of parent and daughter nuclides in a system, it is possible to use radioactive decay in a variety of different methods to determine the age of materials. The mass m of radioactive atoms can be calculated from their activity A , their nuclide mass M , their half-life, and Avogadro's number $N_{Av} = 6.022 \times 10^{23}$:

$$m = \frac{AM}{N_{Av} \ln 2} t_{1/2} \quad (9)$$

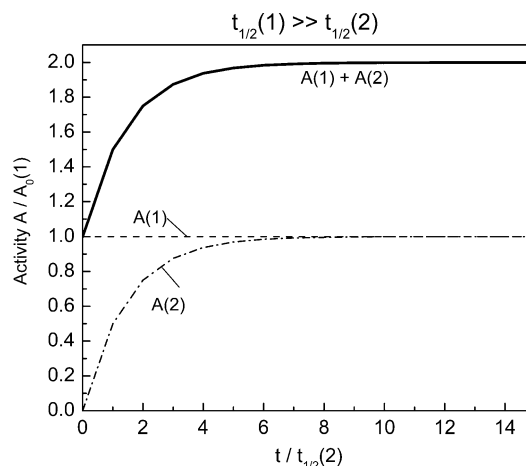


Fig. 3 Activities $A(1)$ of nuclide 1, $A(2)$ of nuclide 2, and sum of activities when the half-life of the parent nuclide is much larger than the half-life of the daughter nuclide. Activities are normalized to the initial activity of the parent nuclide. The timescale is normalized to the half-life of the daughter nuclide. Secular radioactive equilibrium, i.e., parent and daughter have same activities, is achieved after a time equivalent to approximately eight half-lives of the daughter

Radioactive Decay Series

When a parent nucleus decays, it may decay into another radioactive nucleus. As a result, the original parent nuclide can produce a series of related nuclides which are referred to as a radioactive decay series (see “► [U-Series Dating](#)”). A famous example is the decay series of $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$ (also known as the uranium-radium series). The mass number of $^{238}_{92}\text{U}$ is 238 which can be written as $4n + 2$ ($n = 59$). By variation of n all possible mass numbers in the uranium-radium series can be obtained, which is therefore often labeled $A = 4n + 2$. Other examples are $^{235}_{92}\text{U}$ to $^{207}_{82}\text{Pb}$ (uranium-actinium series, with mass numbers $A = 4n + 3$) and $^{232}_{90}\text{Th}$ to $^{208}_{82}\text{Pb}$ (mass numbers $A = 4n$).

Some nuclides can decay in two different ways, such as $^{212}_{83}\text{Bi}$ that has two daughter nuclides: $^{212}_{84}\text{Po}$ via β^- -decay and $^{208}_{81}\text{Tl}$ via α -decay. Thus within each decay series there may be multiple pathways to reach the last member of the series. Half-lives can vary considerably within one decay series. Extreme examples are $^{232}_{90}\text{Th}$ with a half-life of 1.4×10^{10} year and $^{212}_{84}\text{Po}$ with a half-life of 0.3×10^{-12} s in the same decay series. Figure 2 shows the complete thorium decay series with type of decay and half-life for each nuclide.

Radioactive Equilibria and Disequilibria

In a decay series nuclides are transformed into each other:

nuclide 1 $\rightarrow$ nuclide 2 $\rightarrow$ nuclide 3 $\rightarrow$...

Nuclide 2 (N_2) is produced through the decay of nuclide 1 (N_1), but decays simultaneously at a different rate into nuclide 3. The production rate of nuclide 2 is given by the decay rate of nuclide 1 diminished by the decay rate of nuclide 2.

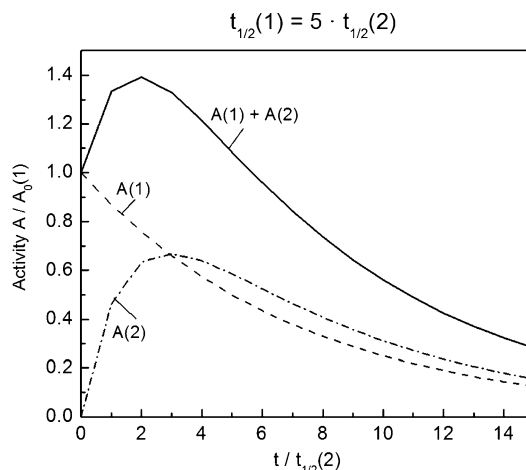


Fig. 4 Activities $A(1)$ of nuclide 1, $A(2)$ of nuclide 2, and sum of activities when the half-life of the parent nuclide is five times the half-life of the daughter nuclide. Activities are normalized to the initial activity of the parent nuclide. The timescale is normalized to the half-life of the daughter nuclide. Transient radioactive equilibrium is achieved when the ratio of parent and daughter activities is constant

In a system where initially only the parent nuclide N_1 is present, daughter nuclides build up over time. Eventually an equilibrium state will be reached, where the ratio of the numbers of nuclei N_1/N_2 is constant.

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1 \quad (10)$$

The time necessary to attain this radioactive equilibrium depends on the decay constants of the two nuclides. Two important cases include systems where the mother nuclide has a much longer half-life than the daughter and systems where the half-lives are comparable.

Secular radioactive equilibrium refers to cases where the half-life of the parent nuclide is much larger than that of the daughter: $t_{1/2}(1) \gg t_{1/2}(2)$. In secular radioactive equilibrium, the activities of the parent nuclide and the daughter nuclide are the same. A prominent example is the decay of ^{226}Ra (1,600 years) to ^{222}Rn (3.825 days). The gaseous radon is easily separated from its parent nuclide. Once radon is prevented from escaping, radioactive equilibrium will be established after about eight half-lives of the daughter nuclide, i.e., approximately 1 month (compare Fig. 3). In equilibrium ^{226}Ra , ^{222}Rn , and all other short-lived daughter nuclides have the same activities.

Transient radioactive equilibrium can be attained when the half-life of the parent nuclide is larger than that of the daughter, but the decay of the parent nuclide cannot be neglected: $t_{1/2}(1) > t_{1/2}(2)$. Once equilibrium is established, the activity of the daughter nuclide is larger than that of the parent nuclide (compare Fig. 4). The ratio of the activities is constant.

As the difference between the half-lives becomes smaller, the time required to reach equilibrium increases continuously. If the half-life of the parent is shorter than that of the daughter, no equilibrium can be attained.

Radioactive equilibria have several practical applications. By measuring the activity of the daughter nuclides, the activity of the parent nuclide can be determined, e.g., the amount of ^{238}U in a sample can be determined by measuring the activity of ^{234}Th . Alternatively, if activities of parent and daughter nuclides can be measured, it is possible to determine if an equilibrium state has been attained. A deviation from the equilibrium state, i.e., a disequilibrium, points toward transport of

nuclides into or out of the system. Nuclides of the decay series can be separated by natural processes if parent and daughter have different chemical behavior (e.g., uranium is soluble, thorium is particle adhesive) or if they have different probabilities of escape (the gas radon has a very high probability to escape out of a system). Recoil due to α -decay can lead to lower binding of daughters such as is the case for ^{234}U and ^{238}U .

Interaction of Radiation with Matter

Ionizing radiation can be divided into three groups – charged particles (heavy charged particles and electrons), photons, and neutrons – each of which has different mechanisms of interacting with matter.

Heavy charged particles, i.e., protons and heavier nuclei such as α -radiation, interact predominantly through coulomb forces between their positive charge and the negative charge of the electrons in the material being traversed. This leads to ionization and excitation of the target atoms. Energies required for the ionization process are on the order of several eV, i.e., the energy of visible and ultraviolet light. Radioactive decays produce radiation with energies of 0.1–10 MeV, so that α -particles produce a track with large numbers of ions and electrons. The secondary electrons released in these ionization processes are often energetic enough to cause further ionization and are often referred to as δ -radiation. Some of the charges can become trapped instead of recombining with the ions (see “► [Luminescence Dating](#)”). The ionization density of heavy charged particles is on the order of several thousand ion pairs per mm travelled. It depends on the energy lost per unit distance travelled by the ionizing particle, which is also called linear energy transfer or LET. The LET of heavy charged particles increases with distance travelled and decreases sharply after reaching a peak value, meaning α -particles interact more strongly as their velocity decreases. Due to their large mass, they are not easily deflected and their trajectory is usually a straight line with a well-defined range. A 3 MeV α -particle has a range of 1.7 cm in air and can barely penetrate a sheet of paper.

β -Radiation consists of electrons or positrons and can interact with matter in different ways including ionization and excitation of electrons in the absorbing material. Electrons can also interact with the electric field of positive nuclei under emission of bremsstrahlung. If they move through a substance with a velocity higher than the speed of light in that substance, they emit Čerenkov radiation, which is observed as deep blue light. This light is most commonly seen in open, pool-type reactors. Positrons usually annihilate with electrons in which process two gamma photons of 511 keV are emitted. Opposed to α -particles, electrons are significantly deflected by collisions with other electrons and therefore follow a zigzag path. Their range is less clearly defined. 3 MeV electrons have a range of approximately 20 m in air with an ionization density of ~ 4 ion pairs per mm and can penetrate a few millimeters of aluminum. Electrons with low energies can also experience backscattering in high-Z absorbers so that absorbers of low atomic number such as plastic or aluminum are most effective in absorbing β -radiation.

γ - and X-rays both consist of photons and have similar properties, but are distinguished by their origins: X-rays are emitted by the electron shell of atoms when electrons change from a higher- to a lower-energy orbit (characteristic X-rays) or when electrons (or other particles) are slowed down in the electric field of nuclei (bremsstrahlung). X-ray energies range from 100 eV to 100 keV. γ -Radiation is emitted during de-excitation of a nucleus, and energies range from 10 keV to 10 GeV. While particles usually lose their energy in a succession of collisions, photons mostly lose their energy in a single process. Photons interact in three different ways: In the photo effect the γ -photon

transfers its complete energy to an electron which is then emitted as a photoelectron. In the Compton effect the photon gives off only part of its energy to an electron and is then deflected into a different direction. If its energy is larger than 1.02 MeV, the photon can be transformed into an electron-positron pair (pair production). The probability for each process depends on the energy of the photon and the absorbing material. Due to the probabilistic nature of the interactions, photons have no clearly defined range. They are either removed from a beam or not. Instead of giving a range in a specific material their interaction is usually described by an absorption coefficient or their reduction in intensity: 1 MeV γ -radiation is reduced to an intensity of 1 % by 5 cm of lead or 25 cm concrete.

Neutrons are electrically neutral and interact only very weakly with electrons. They lose energy through collisions with nuclei. The neutron transfers part of its energy to the nucleus and changes its direction. This process is called scattering and leads to a slowing down of the neutrons. Scattering is most efficient in materials that contain a high amount of hydrogen, such as paraffin. Neutrons can also be absorbed by a nucleus (neutron capture). This process can lead to the formation of a stable or unstable nucleus and is used in neutron activation where radioactive nuclides are created by bombardment with neutrons (see “► [Neutron Activation Analysis](#)”). Neutrons are classified by their energy. Thermal and slow neutrons (energies >0.1 eV and 0.1–100 eV, respectively) are effectively captured by nuclei. Thermal neutron scattering is used for material characterization. Fast neutrons (0.1–10 MeV) typically lose their energy through a series of scattering events which can lead to recoil or excitation of the target nucleus. There is also a small probability for fast neutron capture. Neutrons with energies >10 MeV can cause spallation when colliding with a nucleus, in which process the target nucleus emits several nucleons with the result of leaving a lighter nucleus.

Measurement of Radiation and Radiation Dosimetry

Radiation is detected through its interaction with matter. Different methods include the ionization of gases or semiconductors and excitation of scintillators.

1. In gas-filled detectors radiation creates a trail of ion pairs. Ions and electrons are separated by applying an electric field and give rise to a current. This process is used in ionization chambers which are most effective for α - and fission fragments, proportional counters which allow quantitative measurement of α - and β -radiation, or Geiger-Muller counters for high-energy β - or X-rays (see “► [Beta Counter](#)”).
2. Scintillation detectors consist of transparent solids or liquids which emit photons when radiation is absorbed. The emitted photons are subsequently measured. Examples include NaI(Tl), CsI (Tl), and ZnS(Ag). Scintillation counters are more efficient detectors for γ -radiation than Geiger-Muller counters and are also suitable for α - and β -radiation.
3. Semiconductor detectors, such as high-purity Germanium crystals, are widely used for γ - and X-ray spectroscopy. Radiation creates charge carriers which are separated by an electric field. They are able to produce further electron hole pairs, creating an electric pulse. The pulse height is proportional to the energy of the γ -photon.

Detectors of types 2 and 3 are frequently used for spectroscopy of α - and γ -radiation to allow identification of radionuclides (see “► [Alpha Spectroscopy](#)”). Germanium detectors and NaI(Tl) scintillators are commonly used for gamma spectroscopy while alpha spectroscopy is carried out

with silicon surface barrier detectors. Due to the continuous nature of β -particles beta spectroscopy is less frequently applied. X-ray spectroscopy is carried out with Si(Li) detectors.

Other detectors such as photographic film and luminescence detectors are based on trapped electrons created by the passage of radiation. These detectors are commonly used for radiation dosimetry. Radiation dosimetry quantitatively relates radiation exposure and resulting physical, chemical, or biological changes. The primary physical quantity used is the absorbed dose. It describes the energy deposited by radiation per kg mass. Units used for dose are the SI-unit gray (Gy) and the rad:

$$1 \text{ gray} = 1\text{Gy} = 1 \text{ J/kg} = 100 \text{ rad}$$

“► [Luminescence Dating](#)” is based on measurement of absorbed dose.

Types of Nuclides

Radiation and radioactivity form the basis of many dating methods for which applications different types of nuclides and their origins have to be distinguished.

Primordial nuclides have been present from early times of the universe (see “► [Extinct Radionuclide Dating](#)”). During early stages of the universe, light elements such as H, He, Li, and Be (number of nucleons $A \leq 7$) formed in primordial nucleosynthesis. After the formation of stars, fusion processes in stellar nucleosynthesis resulted in nuclides with $A \leq 60$. Nuclides with $A > 60$ formed through neutron capture. Some of these primordial nuclides are radioactive. **Radiogenic nuclides** can be stable or radioactive and result from the decay of a parent nuclide.

The number of radioactive nuclides varies over time and their variation can be described by the laws of radioactive decay. While the concentration of the parent nuclide(s) decreases, the concentration of stable decay products increases. The decay constants are known (see “► [Radioactive Decay Constants, A Review](#)”). This forms the basis of a variety of nuclear dating methods. Suitable timescales depend on the half-lives. Examples for terrestrial parent-daughter pairs used in dating are $^{40}\text{K}/^{40}\text{Ar}$ (see “► [Ar–Ar and K–Ar Dating](#)”), $^{87}\text{Rb}/^{87}\text{Sr}$ (see “► [Rb–Sr Dating](#)”), $^{147}\text{Sm}/^{143}\text{Nd}$ (see “► [Sm–Nd Dating](#)”), $^{176}\text{Lu}/^{176}\text{Hf}$ (see “► [Lu–Hf Dating](#)”), and $^{187}\text{Re}/^{187}\text{Os}$ (see “► [Re–Os Dating](#)”).

When using these pairs it is important to take into account that daughter nuclides might already be present at $t = 0$. Usually a stable isotope of the daughter nuclide is used to calibrate initial concentrations of the decay product (see “► [Ar–Ar and K–Ar Dating](#)”).

A similar approach is used for nuclides in natural decay series. If parent and daughter nuclides show different chemical behaviors, radioactive disequilibria can be used to determine the date of separation. It is important to determine if a system is closed or open, i.e., to ensure that no losses have occurred. See for comparison “► [\$^{210}\text{Pb}\$ Dating](#),” “► [\$^{226}\text{Ra}\$ Dating, Sediment](#),” “► [U-Series Dating](#),” “► [U–Th:He Dating](#),” and “► [Uranium-Lead Dating](#).”

Nuclides in the uranium and thorium chains are also used for “► [Fission Track Dating](#)” and alpha-recoil track dating. Spontaneous or induced fission of heavy nuclei, mainly ^{238}U , can leave tracks in solids that can be made visible under a microscope by treatment with chemicals. Similarly, recoiling of atoms due to α -decay can leave a track. The track density depends on the concentration of ^{238}U and other nuclides and the time elapsed.

Another large group of nuclides that are used for dating are of cosmogenic origin (Lal 2000; Gosse and Phillips 2001; see “► [Cosmogenic Nuclide Dating](#)”). **Cosmogenic radionuclides** are continuously formed by the interaction of cosmic rays with the atmosphere and the Earth’s surface.

Cosmic radiation includes galactic cosmic rays and solar energetic particles. The galactic cosmic ray spectrum consists of approximately 85 % protons, 12 % alpha particles, 1 % heavier nuclei, and about 2 % electrons and positrons (Benton and Benton 2001). The energies range from several 10 up to 10^{12} MeV with a broad peak between 0.1 and 1 GeV. Solar energetic particles include electrons, protons, and heavier ions, and ~ 50 events can be expected in the 11-year solar cycle (for a detailed description Benton and Benton 2001).

Primary cosmic rays interact with the atmosphere and have been completely attenuated at 20 km height. They cause spallation reactions and result in secondary protons, neutrons, and muons. These secondary particles lead to further nuclear reactions in the atmosphere and can even reach the surface. In the process new nuclides are formed which can be radioactive (^3H , ^{14}C , ^{10}Be , ^{26}Al , ^{32}Si , ^{36}Cl , ^{39}Ar , ^{41}Ca , ^{81}Kr) or stable (^3He and ^{21}Ne). Prerequisite for dating based on cosmogenic nuclides is the knowledge of production rates over the time span to be dated.

Summary

The decay of primordial and radiogenic nuclides and the production of cosmogenic nuclides form the basis of various dating methods. Radioactive decay can be described by an exponential decay law. The radiation emitted in the decay process can be used to characterize the nuclides present in a system and to determine their concentrations. Radiation is detected through the interaction processes with the material it traverses.

Cross-References

- ▶ [1⁴C Dating](#)
- ▶ [2¹⁰Pb Dating](#)
- ▶ [2²⁶Ra Dating, Sediment](#)
- ▶ [4He/³He/³He Dating](#)
- ▶ [Alpha Spectroscopy](#)
- ▶ [Ar–Ar and K–Ar Dating](#)
- ▶ [Beta Counter](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Extinct Radionuclide Dating](#)
- ▶ [Fission Track Dating](#)
- ▶ [Lu–Hf Dating](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Neutron Activation Analysis](#)
- ▶ [Radiation Defect](#)
- ▶ [Radiation Dose Rate](#)
- ▶ [Radioactive Decay Constants: A Review](#)
- ▶ [Rb–Sr Dating](#)
- ▶ [Re–Os Dating](#)
- ▶ [Sm–Nd Dating](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [U-Series Dating](#)
- ▶ [U–Th:He Dating](#)

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Luminescence, Martian Sediments

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Synonyms

[Martian regolith](#)

Introduction

Mars is the most Earthlike planet of the solar system and the planet most likely to have hosted life. The Martian surface exhibits abundant evidence of having undergone a complex geologic and climatic evolution. Aeolian, fluvial, periglacial, and volcanic processes appear to have remained active through to the present day, and evidence even points to active global climate change (Carr 2006). Luminescence dating has been suggested as one method to provide a chronology for Martian surface regolith, and efforts are underway to develop a robotic instrument for an in situ mission. Differences between terrestrial and Martian environments influence the dating methodology and the instrumentation required.

Mineral Composition

Unlike with terrestrial applications, an in situ luminescence dating instrument for Martian regolith samples will likely not allow chemical treatment and mineral separation. Work with polymineralic samples is a prerequisite. Data obtained by the thermal emission spectrometer distinguish two different types of regolith on Mars, namely, basaltic and andesitic, which are composed of plagioclase feldspars, pyroxenes, and hematite (Bandfield et al. 2000; Bandfield 2002). Plagioclase feldspars are found to have a calcium content of 30–70 % (Milam et al. 2004). Observations by the Spirit and Opportunity rovers further revealed a wide variety of minerals (Chevrier and Mathe 2007), some of which are believed to have formed under the influence of water. Luminescence studies used a variety of Martian simulants to approximate the type of polymineralic samples that may be found on the Martian surface, including the Martian soil simulant JSC Mars-1 (Lepper and McKeever 2000; Banerjee et al. 2002), various minerals and mineral mixtures (Kalchgruber et al. 2006; Jain et al. 2006; Blair et al. 2007; DeWitt and McKeever 2011; O'Connor et al. 2011), or basalt (Tsukamoto et al. 2011).

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Measurement Procedures and Fading

In situ luminescence dating procedures for Martian regolith are limited by the polyminerallc nature of the samples and the small amounts of sample material that can be measured under the given power constraints. Kalchgruber et al. (2006) and Blair et al. (2007) found the “single-aliquot regenerative-dose” (SAR) technique suitable for polyminerallc samples. DeWitt and McKeever (2011) using mineral mixtures found that over 80 % of the blue-stimulated OSL and almost 100 % of the IR-stimulated OSL signals come from the feldspar components, so that anomalous fading is of concern. Fading can be minimized by using thermoluminescence, IR stimulation and detection in the blue wavelength range, detection of red emissions, pulsed stimulation, or IR stimulation at elevated temperatures (Jain et al. 2006; Tsukamoto and Duller 2008; Morthekai et al. 2008).

Solar Resetting

A basic premise of OSL dating is that the sediments to be dated have been exposed to sufficient amounts of light at the time of deposition to erase any previously accumulated signal. In terrestrial applications, this “zeroing” of the signal is accomplished within a few minutes of exposure to sunlight (Aitken 1998). Modeling of radiation transport in the Martian atmosphere suggested a more intense UV component at the Martian surface than is found on Earth (McKeever et al. 2006), and this may lead to different bleaching efficiencies. Carrying out experiments with a Mars solar simulator and detecting the UV luminescence, Kalchgruber et al. (2007) found efficient bleaching of the IR-stimulated signal from mineral mixtures after exposure for 1 h. When blue stimulation was used, the authors observed a non-bleachable residual signal, which was approximately 5 % of the original signal. Detschel and Lepper (2009) tested the influence of UV and a simulated Martian spectrum on the luminescence of various samples. They found that Na-feldspar (albite) tends to acquire an OSL signal with increasing UV exposure and might pose a challenge to optical dating. Ca- and K-feldspars did not acquire a significant signal under UV exposure and could be bleached when exposed to the simulated Martian spectrum. Both authors conclude that luminescence dating of Martian regolith should not be compromised by the UV-enhanced solar spectrum.

Temperature Dependence

On Earth, most minerals that are dated by OSL are found in conditions where the temperatures vary annually over a maximum range of perhaps 50 K for the entirety of their storage period. On Mars, the average ambient temperature is much lower with much larger diurnal and annual variations. Temperatures can fluctuate by 80 K within 1 day (Kieffer 1976; Hansson 1997). The global variation is reported to be from 140 to 300 K (Kieffer et al. 1992). Low-temperature OSL measurements and computer simulations indicate that known doses delivered at low temperatures can be effectively estimated if the stimulation temperature is greater than the highest temperature during irradiation (Blair et al. 2006; McKeever et al. 2010). An in situ OSL instrument must therefore provide a heating option to temperatures at least as high as 380 K.

Radiation Environment

Another challenge is the radiation environment encountered at the surface and in the regolith of Mars. Radioactive nuclides (U, Th, and K) play only a minor role in the near-surface deposits on Mars, and available data from the Mars Odyssey Gamma-Ray Spectrometer (Boynton et al. 2004; Wänke et al. 2005) will be sufficient to determine the resulting dose rate background. The primary radiation field on Mars is from galactic cosmic rays (GCR) and solar energetic particles (SEP). The GCR spectrum consists of approximately 85 % protons, 12 % alpha particles, 1 % heavier nuclei, and about 2 % electrons and positrons. The energies range from several tens up to 10^{12} MeV with a broad peak between 0.1 and 1 GeV. Solar energetic particles include electrons, protons, and heavier ions, and ~50 events can be expected in the 11-year solar cycle (for a detailed description, see, e.g., Benton and Benton 2001). This is a significant difference compared to Earth.

The efficiency of OSL signal production varies with the type of radiation. Specifically, low-energy high-Z particles have a high ionization power or large linear energy transfer (LET). Such particles are not as efficient in producing OSL signals. The high ionization density in the track of the particle as it traverses through the material leads to local saturation of the signal (Jain et al. 2006, 2007; Kalchgruber et al. 2007). The composition of the radiation and, therefore, LET change with depth due to scattering and absorption of the particles.

In terrestrial applications, ^{90}Sr beta sources are commonly used for determination of the dose response. Corrections are applied to allow for the smaller luminescence efficiency of alpha radiation compared to beta radiation. Similar corrections will be necessary when the luminescence produced by energetic particles in the cosmic radiation is compared with the calibration radiation source onboard the robotic instrument. However, cosmic ray spectra are dominated by the lower LET parts of the spectrum such that the absorbed dose is primarily (95 %) from high-energy protons and He ions. For such low-LET irradiations, the luminescence efficiency is ~1, with respect to ^{60}Co or ^{90}Sr radiation, introducing only a small error.

Dose Rate

Dose rates on the Martian surface depend upon altitude. Numbers quoted by authors vary but are of the order ~80–120 mGy/year (Saganti et al. 2004) and 43–51 mGy/year (McKeever et al. 2003; Banerjee and Dewangan 2008). The intensity and composition of the cosmic radiation field will change with increasing depth in the regolith due to absorption and scattering. At a depth of 25 g/cm², the dose rate is estimated to be 200 mGy/year, while at 700 g/cm² the dose rate is expected to be reduced to approximately 0.5 mGy/year (Pavlov et al. 2002; see also McKeever et al. 2003), which is an order of magnitude lower than the 2–12 mGy/year natural radioactivity on Earth. Various authors have carried out model calculations to determine dose rate versus depth (Dartnell et al. 2007; Mortheikai et al. 2007; Banerjee and Dewangan 2008).

Anticipated Age Limits and Uncertainties

Assuming a lower measurable dose limit of 5 Gy (Kalchgruber et al. 2007) and an average surface dose rate of 100 mGy/year (Saganti et al. 2004), the lower age limit for OSL dating can be expected to be a few decades. With an upper measurable dose limit of 1,500 Gy, the upper age limit would be only 10,000 years and, thus, considerably lower than on Earth. However, the dose rate decreases

rapidly with increasing burial depth. At 3–4 m depth and a background dose rate of 0.5 mGy/year, the upper age limit would be 3 Ma. Depending on the burial rate, the upper age limit is, therefore, expected to be in the region of several 10^5 years. Dose rate variations with depth depend on the model used but are in the range of 50 % for 2 m burial depth (McKeever et al. 2003; Morthekai et al. 2007). For an initial approximation, the age can be bracketed by calculating a minimum age based on the surface dose rate and a maximum age based on the dose rate at the depth from which the sample is recovered. An improved age value can then be determined using burial models.

Instrumentation

Robotic instrumentation for a space mission has to meet strong specifications, some of them regarding volume (max. 1,000 cm³), weight (max. 0.6 kg), power consumption (max. 10 W), and temperature range (−20 °C to 40 °C). Designs for in situ instrumentation have been suggested by Botter-Jensen et al. (2010) and DeWitt and McKeever (2011).

Both instruments use photomultipliers for detection, various light sources for stimulation, a heating element, and a miniature X-ray source for calibration of the measurements.

Summary

Luminescence dating is a suitable method to provide a chronology for Martian surface materials. The use of a robotic luminescence dating instrument for Mars requires the development of new measurement techniques in order to deal with the multiple new challenges of the Martian environment not usually found when using OSL to date terrestrial sediments. The challenges are posed, among others, by the mineral composition, the sunlight spectrum, and the radiation environment.

Cross-References

- [Luminescence Dating](#)
- [Luminescence Dating, Dose Rate](#)
- [Luminescence Dating, Uncertainties, and Age Range](#)
- [Radiation and Radioactivity](#)

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Luminescence, Rock Surfaces

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Definition

Luminescence is the light emitted following the release of stored energy (in the form of trapped charge) accumulated in crystalline materials; this energy accumulates in natural minerals such as quartz and feldspar through the absorption of ionizing radiation, either cosmic rays or resulting from the decay of naturally occurring radionuclides. This trapped charge can be released or reset by heat or light; if reset by heat, the light emitted from the mineral is called thermoluminescence (TL), and if released by photon stimulation, it is called optically stimulated luminescence (OSL). Thus, luminescence dating provides an estimate of the time elapsed since the mineral grains were last heated or exposed to daylight (Aitken 1998).

Introduction

In geology and archaeology, there are many examples of rock surfaces, rock art, and stone structures of unknown age. In archaeology, megaliths, buildings, chambered burial mounds, field walls, and cairns are very important to understanding the way in which people have used the landscape (Liritzis et al. 2013). In geology, there are examples of ice-scoured bedrock, ice-transported rocks (erratics), and cobble fans from extreme fluvial events whose ages are essential for understanding the evolution of the driving climate-related phenomena.

Luminescence dating is a well-established method of absolute chronology that has been successfully applied to a wide range of fine-grained sediments to provide depositional ages from a few years (Madsen and Murray 2009) to several tens of thousands (e.g., Murray and Olley 2002; Duller 2004) and even several hundred thousand years (e.g., Watanuki et al. 2005; Wang et al. 2006; Porat et al. 2010; Buylaert et al. 2012). The luminescence age of a sample is calculated by dividing the amount of ionizing radiation the sample absorbed during burial (measured as the equivalent dose, D_e) by the rate of energy absorption (the dose rate) from the environment. The single-aliquot regenerative dose (SAR) procedure is the standard approach to D_e determination in quartz and feldspar (Murray and Wintle 2000; Wallinga et al. 2000; Auclair et al. 2003; Buylaert et al. 2012). Dose rate calculations are dependent on the spatial distribution of energy deposition rates by the various radiations (α , β , γ). Aitken (1985) outlines an approach to such calculations near interfaces (including buried rock surfaces), although later authors suggest that the details of this approach may require modification (Yang et al. 1998).

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Development of the Luminescence Dating of Rock Surfaces

Early attempts to date buried rock surfaces used the TL signal from calcitic rocks; this approach was based on the idea that the signal was lost as a result of exposure to daylight before burial. Liritzis (1994) proposed the use of TL to date the construction of a megalithic limestone building. Similarly, attempts were made to determine the ages of the Apollo Temple at Delphi (Liritzis et al. 1997) and of limestone pyramids in Greece (Theocaris et al. 1997). However, even after long exposures to sunlight, a significant residual TL signal remains (Liritzis and Galloway 1999); this significantly limits the youngest ages that can be determined using this method. To circumvent this problem, later studies investigated the potential of the OSL signal; it was known from the earliest days of sediment dating that this signal bleaches much more quickly and to a much lower level than TL signals (e.g., Huntley et al. 1985). First attempts were reported by Huntley and Richards (1997) in which they tried to determine the burial age of quartzite pebbles using OSL. They showed that there can be sufficient light penetration for OSL dating to be used on a surface layer. However, for most of their samples, the quartz gave so little luminescence in response to optical stimulation that their attempts to obtain reliable equivalent doses did not succeed. Trying to develop a nondestructive surface dating method, Habermann et al. (2000) built a new measurement instrument with which they measured an infrared-stimulated luminescence (IRSL) signal from the surface of a granitic rock; they related this to the dose accumulated since the last exposure to light. They also showed that almost complete bleaching to a depth of at least 2 mm can result from only a few minutes of exposure to sunlight. Morgenstein et al. (2003) used IRSL to date the fine-grained feldspar fraction scraped off the uppermost part from the bleached surface of lithic artifacts. However, the ages they obtained were not in agreement with the available age controls. They attributed this to anomalous fading (unexpected loss of signal due to quantum tunneling phenomenon in feldspars) and partial bleaching of feldspar grains. Following the idea proposed by Habermann et al. (2000), Greilich et al. (2005) used a high-spatial-resolution detection technique (HR-OSL) for OSL based on a CCD camera system to date a stone wall of the medieval castle of Lindenfels in southwestern Germany and the pre-Columbian Nasca lines (geoglyphs) around Palpa in southern Peru. Using the infrared-stimulated yellow emission from their samples, they obtained some ages in agreement with archaeological age control. However, they did not take into account anomalous fading which is known to be very common (if not universal; Huntley and Lian 2006) in the IRSL signals from feldspars. Vafiadou et al. (2007) obtained useful signals from granitic rocks using the blue stimulated ultraviolet (UV) signal originating from whole rock slices and reported complete daylight bleaching up to a depth of 5 mm after 14 days of exposure to sunlight for all of their samples. More studies on the application of TL and OSL signals to rock surfaces from archaeological sites have been carried out by Liritzis et al. (2007, 2008, 2010); however, none of these are supported by independent age control. Liritzis (2011) reviews most of these studies of luminescence rock surface dating. Simms et al. (2011) tried to reconstruct sea levels in Antarctica by measuring OSL from quartz grains obtained from the underside of cobbles within raised beaches and boulder pavements. The ages they obtained were internally consistent and agreed with radiocarbon ages. However, their quartz grains were contaminated with feldspar and they had to take into account both fading and internal dose rate (Simms et al. 2011).

In a very different approach, Polikreti et al. (2003), Polikreti (2007) suggested the possibility of using luminescence to estimate the length of time a rock surface was exposed to daylight; this would give similar information to that obtained from cosmogenic nuclide (CN) dating. While looking for a method to determine the authenticity of marble artifacts of disputed age, they investigated the bleaching of the TL signal with depth in several samples and developed a model

to describe the dependence of TL intensity on exposure time and depth; however, they were unable to estimate values for parameters in their model and so could not quantify the exposure time. Sohbaty et al. (2011) studied the depth dependence of the bleaching of the IRSL signal from granitic rocks. Using some simplifying assumptions, they presented a model of this dependence and showed it to be a good descriptor of the remaining luminescence in their naturally exposed samples. According to their model, the longer the exposure time, the further into a rock surface the luminescence is reset. However, they were unable to determine realistic estimates for some of the parameters in the model from first principles, and they did not have any sample of known exposure history with which to calibrate their model. Shortly afterward, Laskaris and Liritzis (2011) proposed a mathematical function to describe the attenuation of daylight into rock surfaces. However, their suggested approximation depends on the assumption that the residual luminescence as a function of depth into rock surfaces has a log-normal distribution, an assumption for which there does not appear to be any physical basis.

Sohbaty et al. (2012a) overcame the problem of parameter estimation by using a known-age roadcut sample for calibration. They then used the resulting parameter values to estimate the exposure times of samples of unknown age. One of their samples was a buried rock surface on which pigment from an extant rock painting was found. They were able to model the distortion in the OSL-depth resetting profile resulting from subsequent burial. This allowed them to determine a pre-burial exposure period age for their sample. This study was the first to report credible exposure ages obtained using OSL surface exposure dating. In a related study, Chapot et al. (2012) derived a burial age for the same sample by dating the outer 1-mm surface of the buried boulder. This age was supported by the OSL age of single grains of sediment buried under the boulder and by the ^{14}C age of a leaf buried between the boulder and the underlying sediment. Together, the two studies constrained the age of the Great Gallery, an archaeologically significant Barrier Canyon Style (BCS) rock art in Canyonlands National Park, Utah, USA.

As a part of an investigation into the burial age of an alluvial cobble pavement at an archaeological site in Portugal, Sohbaty et al. (2012b) further developed their model to include the environmental dose rate. The new model successfully described the variation of dose with depth and time into a quartzite cobble and allowed them to identify and quantify four events (two light exposures of different durations and two sequential burial periods) in the dose record contained within a single clast. Sohbaty et al. (2012b) showed that, for the first time, prolonged periods of exposure can leave a distinct bleaching record in the luminescence/dose profile with depth into a rock surface and, thus, that it may be possible to identify and date multiple deposition events in one sample.

In their model, Sohbaty et al. (2012b) assume that, during daylight exposure, the rate of trapped charge accumulation from natural ionizing radiation was negligible compared to the rate of detrapping due to daylight bleaching. However, they discuss that this assumption is only valid for dating those terrestrial objects which have a short exposure history and a low environmental dose rate. In considering the potential application of their technique in dating non-terrestrial surfaces, where environmental dose rates can be orders of magnitude greater than that on Earth, Sohbaty et al. (2012c) further developed the OSL surface exposure dating model by including the simultaneous effect of daylight bleaching and environmental dose rate. This now represents the most complete model of OSL resetting with depth so far presented and has the potential to date non-terrestrial geomorphological features such as fault movements, rockfalls, landslides, volcanic eruptions, and crater impacts, with an upper limit to the method between 10 and 100 ka on, for example, the Martian surface.

Discussion

Despite the recent progress with luminescence dating of rock surfaces, especially the potential application of this method in surface exposure dating, a widely applicable method has not yet been agreed upon. In sample preparation, for example, some favor working with grains extracted from rock surfaces (e.g., Simms et al. 2011; Chapot et al. 2012; Sohbati et al. 2012a), while others prefer to measure 1- to 1.5-mm-thick intact slices cut from the cores drilled into the rock surfaces (e.g., Greilich et al. 2005; Vafiadou et al. 2007; Sohbati et al. 2012b). In part, this is imposed by the nature of the samples and the fact that solid slices cannot be recovered from friable rock types (e.g., Chapot et al. 2012; Sohbati et al. 2012a). However, the significance of the issue goes beyond the physical properties of rocks and sampling methods and appears to be of dosimetric importance; Sohbati et al. (2011, 2012b) report a difference between doses measured from grains and slices recovered from the same surface for two different rock types. Unfortunately, their investigation into the source of this discrepancy did not result in a conclusive answer.

The above problem also relates to the choice of a luminescence mineral. Although quartz is often the preferred dosimeter in sediment dating, it is often not sufficiently sensitive when extracted from solid rocks (e.g., Huntley and Richards 1997; Tsukamoto et al. 2011; Sohbati et al. 2011). The intensity of signals from feldspars tends to be much less dependent on geological origin and erosion history, but the dosimetry of K-rich feldspar grains extracted from rocks is complicated because the internal dose rate is very dependent on the original feldspar grain size. The *in situ* grain size information is lost during the crushing process used to separate the grains for measurement. There have been attempts to circumvent this problem by using a nondestructive technique based on high-resolution spatially resolved luminescence detection from whole rock slices at a microscale level (e.g., Habermann et al. 2000; Greilich et al. 2002, 2005). However, dose measurement at the microscale level requires dose rate determination on the same scale for age derivation (Guérin et al. 2013); this is unlikely ever to be routine because it requires complex microdosimetry modeling in rock surfaces to include beta dose rate heterogeneity (see Nathan et al. 2003). This problem does not apply to Na-rich feldspar to the same degree because of the absence of internal radioactivity. Sohbati et al. (2013) investigated the potential application of Na-rich feldspar as a potential luminescence dosimeter for the IRSL dating of rock surfaces. The elevated-temperature IRSL signal at 290 °C that they measured after an IR bleach at 50 °C (pIRIR₂₉₀ signal) in the yellow emission seemed to be the most reliable signal for dating rock surfaces in their study; however, they speculated that higher preheat and stimulation temperatures (i.e., >320 °C and 290 °C for preheat and stimulation temperatures, respectively) may result in an even more stable yellow emission signal from Na-rich feldspar.

Conclusions

Direct luminescence dating of rock surfaces is a viable method for dating various geological and archaeological phenomena, including some that cannot be dated using sediments. Depending on the rock type and the sensitivity of quartz extracted from rock surfaces, quartz OSL and Na-rich feldspar pIRIR yellow signals can be used as reliable and dosimetrically tractable signals in the OSL and IRSL dating of rock surfaces. Unlike most sediments, rock surfaces can be exposed for prolonged periods; such long exposure periods leave a distinct bleaching record in the luminescence/dose profile with depth into a cobble. Thus, the degree of bleaching of a rock surface is

recorded within that surface, and in favorable circumstances, it is possible to identify and date multiple burial and exposure events in one sample.

The new technique of OSL surface exposure dating has considerable potential in the dating of many archaeological and geological features, such as the time of construction of megaliths, agricultural land clearance and enclosure, glacial advances and retreats, phases of erosion, and other geological processes and hazards such as mass wasting and fault scarp movement. The method is also ideally suited to the problem of *in situ* measurement of the age of young ($<10^5$ years) exposed surfaces on non-terrestrial bodies.

Cross-References

- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Luminescence Dating, History](#)
- ▶ [Luminescence Dating, Meteorites](#)
- ▶ [Luminescence, Flints and Stones](#)
- ▶ [Luminescence, Martian Sediments](#)
- ▶ [Luminescence, Volcanic Rocks](#)

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Sm–Nd Dating

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Definition

Samarium–neodymium dating uses the radioactive decay of ^{147}Sm to ^{143}Nd and ^{146}Sm to ^{142}Nd to measure the age of rocks and minerals and to trace and date geochemical processes responsible for the chemical differentiation of the Earth and the terrestrial planets and planetesimals.

Introduction

Introduced to the geochemical and cosmochemical communities in the early 1970s, the Sm–Nd radioactive decay systems have grown into essential tools in geochronology and particularly for the tracing of geochemical processes. A key strength of Sm–Nd dating is that it involves two rare earth elements (REE). The behavior of the REE during geologic processes is relatively well understood because, with the exception of Eu and Ce under some conditions, they all have the same ionic charge of +3 and their ionic radius changes monotonically as a function of atomic number. As a result, their fractionation from one another during silicate rock melting and crystallization is predictable. In addition, the low solubility of REE in water leads them to be relatively immobile during rock weathering and to precipitate rapidly out of seawater once delivered to the oceans by rivers. For this reason, the Nd isotopic composition of sediments precipitated from seawater, such as manganese nodules (Piepgras et al. 1979), serves as an excellent tracer for seawater circulation (Jones et al. 2008).

Because Sm and Nd behave similarly in most geologic processes, are not strongly affected by weathering processes, and diffuse through minerals relatively slowly, the Sm–Nd dating system holds promise of being more resistant to resetting than other dating systems and thus is capable of providing accurate initial formation ages for rocks with complicated metamorphic histories. This promise, in part, has been fulfilled. Forty years of application of the Sm–Nd system, however, has provided a better appreciation that not even Sm and Nd are immune to disturbance by routine geologic processes. While this can be a problem if one is trying to obtain an accurate age for an igneous rock subjected to later metamorphism, the growth of a metamorphic mineral like garnet, one of the few minerals that strongly fractionates Sm from Nd, allows the Sm–Nd system to be an extremely useful tool for determining the time of peak metamorphism in a garnet-bearing rock (see ► [Samarium–Neodymium, Metamorphic Rocks](#)). Applications of the Sm–Nd dating system range widely and touch on many fundamental questions of solid Earth and planetary science. Examples include the following: the time of Moon formation; new estimates for the bulk composition of the Earth; the nature and age of magma ocean differentiation on Earth, Mars, and the Moon; the age of the oldest terrestrial crust; the growth rate of the continental crust; age dating of mafic/ultramafic

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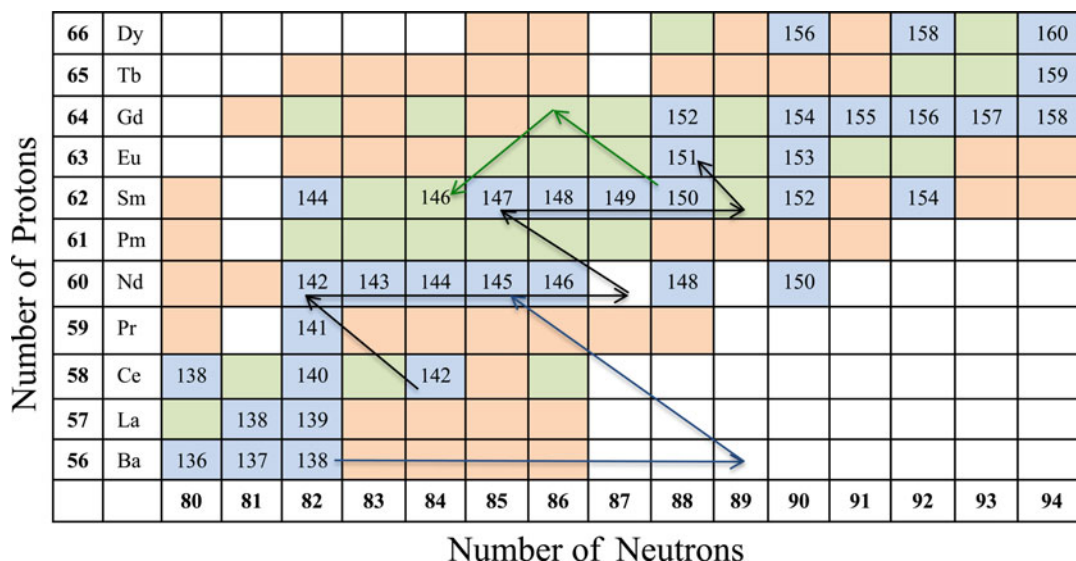


Fig. 1 Portion of the chart of the nuclides in the Sm–Nd mass region. Numbers along the x-and y-axes indicate the number of neutrons and protons, respectively, in each nucleus with the numbers in the boxes showing the combination of neutrons and protons that establish the mass of each nuclide. *Blue boxes* identify stable isotopes. *Green boxes* are isotopes with half-lives ranging from a few days to 10^8 years. *Brown boxes* are nuclides with half-lives ranging from minutes to days. *White boxes* are nuclides with half-lives of less than a minute. The *black arrows* show the path of s-process nucleosynthesis. The *blue arrows* show one path for r-process nucleosynthesis of Nd and the *green arrows* show one path to create ^{146}Sm via p-process nucleosynthesis

rocks; the deformation history of high-grade metamorphic belts; and the patterns of ocean circulation.

Once adequate isotope ratio precisions could be obtained to resolve the radiogenic contributions to ^{143}Nd from the decay of ^{147}Sm , the system could be applied to add a temporal component to the story of REE fractionation by geologic processes that had been developed primarily in the proceeding decade. As the precision of isotope ratio measurements improved further, the even smaller variations in ^{142}Nd due to the decay of the much less abundant, and now extinct, ^{146}Sm came into use for studies of early solar system and planetary processes.

The Nuclear Basics

The REE provide an excellent example of the odd–even effect in nuclear stability. Due to the extra nuclear stability contributed by spin pairing of nucleons, an even number of either neutrons or protons in the nucleus adds to nuclear stability, whereas an odd number of either nucleon decreases nuclear stability. All REE with an even number of protons (Z) have at least four stable or long-lived isotopes, most, including Nd (Z = 60) and Sm (Z = 62), have seven (Fig. 1). The odd-Z REE have between zero (promethium (Z = 61) that does not exist in nature for this reason) and two stable isotopes. Sm and Nd also benefit from having isotopes with 82 neutrons, one of the nuclear “magic numbers” (Mayer 1950) where there is additional stability in the nuclear shell structure model. The effect is apparent in both ^{142}Nd (Z = 60, N = 82) which is the most abundant of the stable Nd isotopes though also lightest in mass, but particularly in ^{144}Sm (Z = 62, N = 82) that is a stable isotope, whereas the next three higher mass Sm isotopes are radioactive with half-lives ranging from 340 days (^{145}Sm) to geologically useful times of 68 Ma (^{146}Sm) and 106 Ga (^{147}Sm).

Table 1 Isotopic composition of Sm and Nd

	¹⁴⁴ Sm	¹⁴⁷ Sm	¹⁴⁸ Sm	¹⁴⁹ Sm	¹⁵⁰ Sm	¹⁵² Sm	¹⁵⁴ Sm
Ratio to ¹⁵² Sm	0.114973	0.56081	0.420430	0.516833	0.275984	1.0	0.850791
Atomic %	0.030746	0.149957	0.112418	0.138201	0.073796	0.267394	0.227486
Atomic weight	143.91200	146.91489	147.91482	148.91718	149.91727	151.91973	153.92221
Atomic weight Sm	150.3653 g/mole						
	¹⁴² Nd	¹⁴³ Nd	¹⁴⁴ Nd	¹⁴⁵ Nd	¹⁴⁶ Nd	¹⁴⁸ Nd	¹⁵⁰ Nd
Ratio to ¹⁴⁴ Nd	1.141842	0.512630	1.0	0.348395	0.7219	0.241583	0.236460
Atomic %	0.271685	0.121973	0.237936	0.082896	0.171766	0.057481	0.056262
Atomic weight	141.90772	142.90981	143.91008	144.91257	145.91311	147.91689	149.92089
Atomic weight Nd	144.2395 g/mole						
Ratio to ¹⁴⁴ Nd	1.138334	0.511845	1.0	0.348927	0.724095	0.243044	0.238595
Atomic %	0.270720	0.121728	0.237821	0.082982	0.172205	0.057801	0.056743
Atomic weight Nd	144.2470 g/mole						

Sm and first-row Nd data from Qin et al. (2011). These Nd data are corrected for instrumental mass fractionation to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219. The second row of Nd data is for the same material, but mass fractionation corrected to ¹⁵⁰Nd/¹⁴²Nd = 0.2096 (DePaolo and Wasserburg 1976b). Atomic masses from Emsley (1991)

The isotopic compositions of Sm and Nd are listed in Table 1. Samarium-147 constitutes just slightly less than 15 atom % of Sm and so is a relatively abundant isotope. In contrast, although ¹⁴⁶Sm was present when planet formation began in the early solar system, it no longer exists in nature because its decay half-life is only 1.5 % of the age of the Earth. Neodymium presents the complication that during the development of the Sm–Nd system, two quite different values were used for mass fractionation during analysis that results in very different measured isotopic compositions for the same Nd (Table 1). In a common technique for Nd isotopic analysis, the sample Nd is loaded onto an electrically heated filament placed in the vacuum of a mass spectrometer (see ► [Thermal Ionization Mass Spectrometer](#)). At temperatures between 1,200 °C and 1,800 °C, the Nd is both evaporated and ionized from the filament. The ionized Nd is then accelerated by an electric field into the mass spectrometer where a large magnet separates the isotopes according to their mass. During evaporation/ionization, the lighter isotopes evaporate preferentially, so the Nd entering the mass spectrometer starts out enriched in light over heavy isotopes compared to the average isotopic composition of the Nd loaded onto the filament. As the analysis proceeds, the heavier Nd isotopes become progressively more abundant. The magnitude of the mass fractionation is on the order of 0.1 % to 2 % per atomic mass unit depending on the measurement technique used. The fractionation would limit isotope ratio determinations to similar precision were it not for the ability to monitor and correct for the fractionation during measurement. The degree of fractionation is determined by comparing the measured ratio of two stable isotopes against some assumed standard value for that ratio. The measured fractionation is then applied to the other isotope ratios using some model of its mass dependency (Carlson 2013). For Nd, the two approaches used assume either ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 (O’Nions et al. 1977) or ¹⁵⁰Nd/¹⁴²Nd = 0.2096 (DePaolo and Wasserburg 1976b) to measure and correct for instrumental fractionation. While the former value produces Nd isotope ratios similar to the values obtained during the first Nd isotope measurements that used the NdO⁺ ion and assumed ¹⁴⁸NdO/¹⁴⁴NdO = 0.242436 (Lugmair et al. 1975b), the latter results in ¹⁴³Nd/¹⁴⁴Nd ratios that are lower by 0.153 % for exactly the same Nd. Care must be taken to compare only data measured using the same mass fractionation correction value or correct the data to the same mass fractionation ratio, in order to accurately compare data from these two data reduction schemes. Fortunately,

the majority of data now reported uses a single fractionation correction value, most commonly $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Given this issue and also to more clearly express the small variations in $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in nature, the isotope ratios are commonly reported as “epsilon” where

$$\epsilon^{143}\text{Nd} = \left(\left(^{143}\text{Nd}/^{144}\text{Nd} \right)_{\text{SA}} / \left(^{143}\text{Nd}/^{144}\text{Nd} \right)_{\text{Chon}} - 1 \right) \times 10^4 \quad (1)$$

and

$$\epsilon^{142}\text{Nd} = \left(\left(^{142}\text{Nd}/^{144}\text{Nd} \right)_{\text{SA}} / \left(^{142}\text{Nd}/^{144}\text{Nd} \right)_{\text{Std}} - 1 \right) \times 10^4 \quad (2)$$

where “SA” is sample, “Chon” is average chondrite (Bouvier et al. 2008), and “Std” is a terrestrial Nd isotope standard, commonly JNdi (Tanaka et al. 2000). Given the very small variations in $^{142}\text{Nd}/^{144}\text{Nd}$, $\epsilon^{142}\text{Nd}$ is sometimes replaced with $\mu^{142}\text{Nd}$, which is calculated as shown in Eq. 2 except with a multiplier of 10^6 instead of 10^4 . Given the isotopic compositions and atomic weights for Sm and Nd listed in Table 1, one can transform the Sm/Nd weight ratio (ppm/ppm) into $^{147}\text{Sm}/^{144}\text{Nd}$ atomic ratio by multiplying the weight ratio by 0.6046 when data are reported relative to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. The multiplier is 0.6049 when Nd data are reported relative to $^{150}\text{Nd}/^{142}\text{Nd} = 0.2096$, another indication of the need for care when comparing results reported from different laboratories that use different mass fractionation corrections for Nd.

As with all elements significantly greater in mass than iron, the REE primarily are made in stellar interiors by adding neutrons to preexisting seed nuclei (Burbidge et al. 1957). This occurs through three routes depending on the neutron density of the stellar site of nucleosynthesis (Truran and Heger 2003). In the latter stages of the life of low- to moderate-mass stars (asymptotic giant branch or AGB stars) when all the hydrogen has been consumed by nuclear fusion in the core of the star, the star contracts and the core density rises until fusion of He begins. As the He is “burned” away to make carbon and oxygen, fusion moves into less dense shells surrounding the core where mixing of material from outside the stellar interior leads to reactions such as the capture of an alpha particle (a ^4He nucleus composed of two protons and two neutrons) by ^{13}C to produce ^{16}O plus a neutron. These neutrons can then be captured by heavier nuclei, which cause them to move to the neutron-rich side of the stable mixture of neutron and protons, the so-called island of β -decay stability (Fig. 1). The more neutron-rich a nucleus becomes, the more likely it is to decay by emitting an electron (β -particle) from its nucleus to transform a neutron into a proton and thus move up in mass along the island of β -decay stability. If the neutron addition occurs more slowly than the decay, the nucleus moves in stair-step fashion up the stable portion of the nuclear chart (Fig. 1). This manner of creating heavier elements is known as slow or s-process nucleosynthesis (Gallino et al. 1997; Busso et al. 2004). For example, the sequential addition of neutrons to ^{142}Nd moves the Nd up in mass through the stable Nd isotopes to ^{146}Nd . Addition of another neutron produces ^{147}Nd , an unstable nuclei with a half-life of 11 days. If no additional neutron comes in during the stability period of ^{147}Nd , it decays to ^{147}Sm , which can capture a neutron to become ^{148}Sm , and so continues to move up mass and Z in the chart of the nuclides (Fig. 1). Because of the relatively short half-life of ^{147}Nd and particularly the 1.7-h half-life of ^{149}Nd , slow neutron addition to Nd has trouble jumping over ^{147}Nd to make stable ^{148}Nd and a particularly difficult time getting past ^{149}Nd to create stable ^{150}Nd .

This is where the second style of nucleosynthesis comes in. If the neutron density gets high enough, for example, in the interior of an exploding star called a supernova, neutron capture occurs

more rapidly than β -decay, so the seed nuclei can be driven to large neutron excesses. Eventually, the half-lives of the neutron-rich isotopes become short enough that, even at these high neutron capture rates, they decay back toward stable nuclei. This more rapid or r-process nucleosynthesis (Cowan and Sneden 2004) is the primary production mechanism for the neutron-rich isotopes of Nd and Sm. The proportion of each Nd isotope created by s-process and r-process nucleosynthetic paths thus changes with mass, with the higher mass Nd isotopes being dominated by r-process production (Arlandini et al. 1999).

The final nucleosynthetic process, the p-process, is responsible for creating the proton-rich isotopes (Meyer and Zinner 2006). In the p-process, energetic photons or neutrinos in a supernova cause the transformation of a neutron into a proton. The unstable proton-rich isotope then decays by either alpha emission or electron capture until it reaches the island of nuclear stability. Both ^{144}Sm and ^{146}Sm are made only by the p-process as neither can be made by the s-process because the s-process path takes ^{146}Nd to ^{147}Sm and both are blocked by stable isotopes of Nd from being produced by the r-process.

The elements now in our solar system consist of a mixture of the elements produced by, and blown off from, individual stars either by mass outflows from AGB stars or from the ejecta of supernova explosions. The importance of this as far as Sm–Nd dating is concerned is that ^{142}Nd cannot be produced by the r-process because β -decay of neutron-rich isotopes will stop at stable ^{142}Ce , which then blocks further decay to ^{142}Nd . If the stellar contributions to Nd in the solar nebula were not perfectly mixed when planet formation began, then variable proportions of s-process and r-process stellar ejecta would cause potentially large variations in the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio in the solar system that are not due to the decay of ^{146}Sm . Nucleosynthetic heterogeneity in the solar nebula is apparent in comparisons of meteorite and terrestrial Nd data (Andreasen and Sharma 2007; Carlson et al. 2007), so this cause of isotopic variation in Nd must be taken into account particularly when applying the ^{146}Sm – ^{142}Nd dating system. The ^{147}Sm – ^{143}Nd system, however, is much less sensitive to this problem, in part because the magnitude of the ^{147}Sm decay contribution to ^{143}Nd is much larger than the ^{146}Sm contribution to ^{142}Nd . In addition, because ^{143}Nd is made by a combination of s-process and r-process nucleosynthesis, its abundance is less sensitive to imperfect mixtures of the two.

Another nuclear feature of the Sm–Nd system that must be appreciated when the Sm–Nd dating technique is applied to extraterrestrial objects is that some Nd and Sm isotopes, particularly ^{149}Sm , have large thermal neutron capture cross sections. When planetary surfaces are exposed to the high-energy particles, mostly protons, known as cosmic rays, the collision of cosmic rays with atoms in the upper meters of the planet/planetesimal can knock neutrons out of the nucleus of the impacted atom. At first, the emitted neutrons will be energetic (epithermal), but collisions with other nearby atoms slow them to thermal energies that allow them to be captured by atoms with large thermal neutron capture cross sections, such as ^{149}Sm (Lingenfelter et al. 1972). On the Moon, the $^{149}\text{Sm}/^{152}\text{Sm}$ ratio can be reduced by more than 0.4 % through neutron capture, raising the $^{150}\text{Sm}/^{152}\text{Sm}$ ratio by about 0.8 % in the process (Rankenburg et al. 2006; Boyet and Carlson 2007; Hidaka and Yoneda 2007). In fact, at least some of the techniques that allowed the development of the Sm–Nd dating system originated from efforts to measure the cosmic ray exposure history of the lunar surface using neutron capture by Sm, and particularly Gd, which has even higher thermal neutron capture cross sections (Eugster et al. 1970; Lugmair and Marti 1971).

With the exception of very minor neutron capture effects in Nd (Rankenburg et al. 2006), neutron capture would have minimal affect on Sm–Nd dating were it not for the fact that the precision needed in Sm/Nd ratio determination is such that the most commonly used technique for

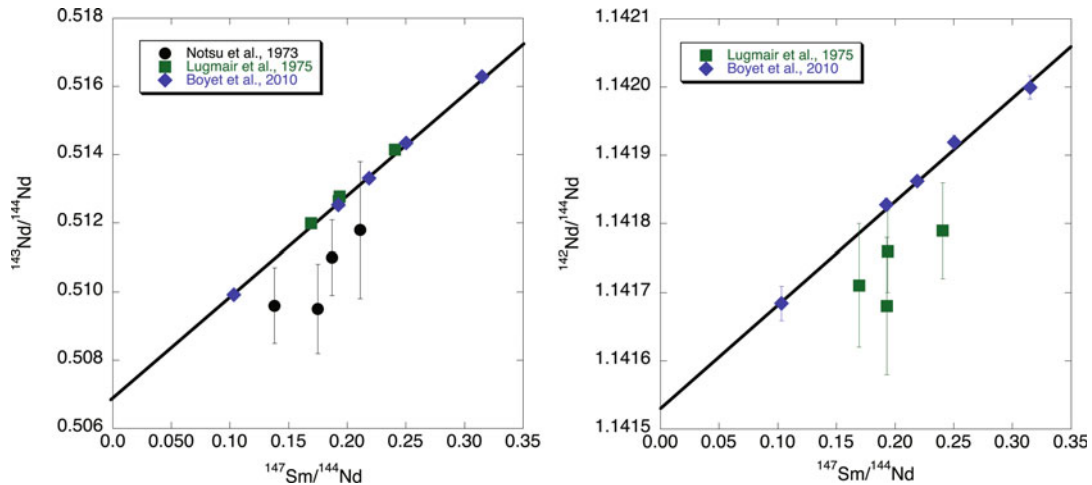


Fig. 2 ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd isochrons for two eucritic meteorites illustrating the need for high-precision isotopic ratio measurements in order to obtain precise isochron slopes. The data from Notsu et al. (1973a) and Lugmair et al. (1975a) are both for the Juvinas eucrite, while the data from Boyet et al. (2010) are for the related eucrite Binda

both Sm and Nd concentration measurement is isotope dilution. In isotope dilution, a known amount of a highly purified isotope of the element is added to a known weight of sample. The degree to which the ratio of the “spike” to some stable isotope of that element in the spike plus sample mixture is changed allows the calculation of the concentration of the element in the sample. Spiking low-abundance isotopes requires less of the often very expensive spike per sample in order to make a precisely measureable shift in isotopic composition, but in the case of Sm, one also aims to avoid potential interference with Nd. For this reason, ^{149}Sm is the most commonly used spike for Sm measurement by isotope dilution. Consequently, one must know the sample’s $^{149}\text{Sm}/^{152}\text{Sm}$ ratio in order to calculate an accurate concentration via this technique. Half a percent depletion in ^{149}Sm due to neutron capture will result in a calculated Sm concentration that is 0.5 % low if the neutron-induced depletion in ^{149}Sm is not taken into account. On Earth, where the atmosphere and magnetic field shield the surface from the majority of cosmic rays, the $^{149}\text{Sm}/^{152}\text{Sm}$ ratio is constant, so neutron capture is not a significant concern for terrestrial Sm–Nd dating.

Sm–Nd Decay Systematics

Both parents ^{146}Sm and ^{147}Sm decay by emitting an alpha particle from their nucleus to end up as daughters ^{142}Nd and ^{143}Nd , respectively. The standard radioactive decay equation for ^{147}Sm – ^{143}Nd dating is

$$\left(^{143}\text{Nd}/^{144}\text{Nd} \right)_p = \left(^{143}\text{Nd}/^{144}\text{Nd} \right)_0 + \left(^{147}\text{Sm}/^{144}\text{Nd} \right)_p \times (e^{\lambda t} - 1) \quad (3)$$

where the subscript “p” refers to present day and “0” to the value at $t = 0$ where t is time. Lambda is the decay constant for ^{147}Sm . For two or more materials formed at the same time and with the same initial Nd isotopic composition, for example, different minerals rapidly crystallized from a homogeneous lava, plotting the two measureable quantities in this equation – $(^{143}\text{Nd}/^{144}\text{Nd})_p$ and $(^{147}\text{Sm}/^{144}\text{Nd})_p$ – against one another will give a line whose slope is equal to $e^{\lambda t} - 1$ and the y-

intercept is the $^{143}\text{Nd}/^{144}\text{Nd}$ at the time of formation of the minerals. The line so obtained is called an isochron (Fig. 2).

Begemann et al. (2001) summarize the measurements of the half-life of ^{147}Sm by radioactive counting. Beginning around 1960, the determinations began to cluster around a mean of 106×10^9 years, which was the value adopted in one of the early Sm–Nd dating studies (Lugmair et al. 1975b) and has been in use ever since. This translates into a decay constant of $6.54 \times 10^{-12} \text{ year}^{-1}$. The value was cross-compared with U–Pb dating of the Stillwater igneous complex by Nunes (1981) who produced a zircon U–Pb age of $2,713 \pm 3 \text{ Ma}$ in comparison with the Sm–Nd isochron age of $2,701 \pm 8 \text{ Ma}$ (DePaolo and Wasserburg 1979) that changes to $2,706 \text{ Ma}$ using the $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ fractionation correction. The overlapping Sm–Nd and U–Pb ages indicate that the ^{147}Sm decay constant currently in use produces ages within 0.5 % of those determined using the U decay system where considerable effort has gone into determining precise decay constants (Begemann et al. 2001). With a 106 billion year (Ga) half-life, the abundance of ^{147}Sm has decreased by only 3 % over the 4.568 Ga history of the solar system.

Until recently, the half-life used for ^{146}Sm was 103 ± 5 million years (Ma) (Friedman et al. 1966), but a more recent experiment derives a significantly shorter half-life of $68 \pm 7 \text{ Ma}$ (Kinoshita et al. 2012). As either half-life is significantly shorter than the age of the Earth, ^{146}Sm no longer exists in measureable quantities in natural materials. Thus, one cannot use the standard radioactive decay equation (3) in order to calculate ages from the ^{146}Sm – ^{142}Nd system. Instead, like all dating systems based on extinct radionuclides, ages from the ^{146}Sm – ^{142}Nd system utilize equations of the form

$$\left(^{142}\text{Nd}/^{144}\text{Nd}\right)\Delta t = \left(^{142}\text{Nd}/^{144}\text{Nd}\right)_0 + ^{146}\text{Sm}/^{144}\text{Nd} \times e^{-\lambda\Delta t} \quad (4)$$

Equation 4 can be expanded as

$$\left(^{142}\text{Nd}/^{144}\text{Nd}\right)\Delta t = \left(^{142}\text{Nd}/^{144}\text{Nd}\right)_0 + \left(^{146}\text{Sm}/^{144}\text{Sm}\right) \times \left(^{144}\text{Sm}/^{144}\text{Nd}\right) \times e^{-\lambda\Delta t} \quad (5)$$

Plotting the two measureable parameters in this equation – $\left(^{142}\text{Nd}/^{144}\text{Nd}\right)\Delta t$ and $\left(^{144}\text{Sm}/^{144}\text{Nd}\right)$ – against one another for a group of minerals formed at the same time and with the same $\left(^{142}\text{Nd}/^{144}\text{Nd}\right)_0$ will give a slope equal to the $^{146}\text{Sm}/^{144}\text{Sm}$ ratio at the time the minerals formed and a y-intercept equal to $\left(^{142}\text{Nd}/^{144}\text{Nd}\right)_0$. Chronologies derived from extinct nuclides thus do not give absolute ages relative to the present day, as in ^{147}Sm – ^{143}Nd , but instead give the abundance ratio of ^{146}Sm to a stable Sm isotope, ^{144}Sm , at the time the material formed. If one rock gives a slope of 0.008 and another a slope of 0.004, then the age difference between the rocks is one half-life of ^{146}Sm , or 68 Ma.

These age differences can be transformed into absolute ages if one knows the $^{146}\text{Sm}/^{144}\text{Sm}$ in the solar system at some well-dated time. For example, if one can measure an accurate ^{147}Sm – ^{143}Nd , or more commonly U–Pb, age for a given sample, then the $^{146}\text{Sm}/^{144}\text{Sm}$ ratio determined for the same sample can serve as a time marker for the declining abundance of ^{146}Sm in the early solar system. This approach is documented in Carlson and Boyet (2009). Using this approach, Boyet et al. (2010) derive a best estimate for the initial $^{146}\text{Sm}/^{144}\text{Sm}$ in the solar system of 0.0084 ± 0.005 at 4.568 Ga. This value, however, was determined using the 103 Ma half-life of ^{146}Sm . Using instead the 68 Ma half-life, the solar system initial $^{146}\text{Sm}/^{144}\text{Sm}$ calculated from the data considered by Boyet et al. (2010) is 0.0094 (Kinoshita et al. 2012). Of concern, and a topic of continuing research, is the question of whether the $^{146}\text{Sm}/^{144}\text{Sm}$ ratio was homogeneous in the solar nebula at the beginning of

Table 2 Melt–solid partition coefficients for Sm and Nd in various minerals

Mineral/basaltic melt	D(Sm)	D(Nd)	References
Olivine	0.00055	0.00022	1
Clinopyroxene	0.462	0.277	2
Garnet	1.1	0.363	2
Garnet	0.18	0.03	3
Clinopyroxene	0.23	0.14	3
Orthopyroxene	0.0056	0.015	3
Plagioclase	0.098	0.123	4
Amphibole	0.28	0.25	5
Phlogopite	0.014	0.012	5
Apatite	12	14	6
Zircon	0.38	0.2	6

The partition coefficient, D, is defined as the ratio of the concentration of the element in the solid compared to melt. References are 1, Beattie (1994); 2, Hauri et al. (1994); 3, Green et al. (2000); 4, Bindeman and Davis (2000); 5, LaTourette et al. (1995); 6, Irving (1978)

planet formation. If ^{146}Sm and other short-lived, recently synthesized radionuclides were injected into the nebula just before the start of solar system formation, then there may not have been enough time for them to have been homogeneously mixed into the nebula prior to the start of planet(esimal) formation. If not, then different $^{146}\text{Sm}/^{144}\text{Sm}$ ratios determined for different rocks could reflect, in part, the heterogeneous distribution of ^{146}Sm in the nebula. Sorting out how much of the variability in the relative abundances of ^{142}Nd in a given rock is due to the possibly heterogeneous initial abundance of ^{146}Sm , or due to different times of rock formation, is not straightforward. The best way to answer this question is to produce a series of ^{146}Sm – ^{142}Nd “ages” for various ancient solar system materials and compare the ^{146}Sm – ^{142}Nd ages with absolute ages determined by long-lived radiometric systems such as ^{147}Sm – ^{143}Nd , U–Pb, Lu–Hf, and Rb–Sr. If the absolute ages indicate the same time span as the relative ages from ^{146}Sm – ^{142}Nd , then the argument is strong that ^{146}Sm was homogeneously distributed in the nebula at the start of planet formation.

At this point, the reader may well be asking “Why bother?” with extinct radionuclide geochronology. The answer is twofold. First, the age precision provided by isochrons is proportional, among other things, to the decay constant, so short-lived radioactive decay schemes have the potential of producing much more precise ages than can be obtained from long-lived radiometric systems. Second, because the parent nuclide becomes extinct early in Earth history, radionuclide decay schemes are less sensitive to modification of parent/daughter ratios that may occur due to metamorphic events occurring long after rock formation and thus can “see through” the later events to provide information on the time of initial rock formation (O’Neil et al. 2012).

The Geochemistry and Cosmochemistry of Sm and Nd

Sm and Nd, and all the other REE, belong to the group of elements known as “refractory lithophile” elements. The “refractory” part means that both elements have high condensation temperatures (Nd = 1,602 °C, Sm = 1,590 °C; Lodders 2003) from a gas of solar composition. As the gaseous solar nebula was cooling after the formation of the Sun, both Sm and Nd were among the first elements to condense into solid grains. Because they have similar condensation temperatures, Sm and Nd should not be dramatically fractionated from one another by condensation or evaporation

processes. The “lithophile” part means that both elements are much more soluble in silicate than in iron (siderophile) or sulfide (chalcophile) melts/solids. As a consequence, a process involving metal–silicate separation, for example, core formation, should not fractionate Sm from Nd as both will stay behind in the silicate mantle. The result of this refractory lithophile behavior of the REE is that most types of primitive meteorites, whose chemistry is controlled largely by volatility and separation of metal from silicate, show a very narrow range of REE relative abundances and a very small range (approx. $\pm 3\%$) in Sm/Nd ratios (Jacobsen and Wasserburg 1980; Boyet and Carlson 2007; Bouvier et al. 2008). For this reason, primitive meteorites often are used to model the refractory lithophile element abundances of the bulk silicate Earth, that part of Earth excluding the core (McDonough and Sun 1995; Palme and O’Neill 2003). The current best estimate for the average $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of primitive meteorites, and hence the solar system, is 0.1960 ± 0.0004 with a corresponding $^{143}\text{Nd}/^{144}\text{Nd} = 0.512630 \pm 11$ (Bouvier et al. 2008).

The most effective natural processes capable of separating Sm from Nd are partial melting and fractionation crystallization. The ability of minerals to fractionate a given element is expressed by their partition coefficient, which is the ratio of the concentration of an element in a mineral compared to the concentration of the same element in a melt with which the mineral is in chemical equilibrium. Table 2 lists the partition coefficients for Sm and Nd in various minerals. Most minerals have low partition coefficients for REE, meaning that the REE tend to be “incompatible” in most silicate minerals. As a result, they selectively partition into the melt during partial melting and concentrate in the residual liquid during fractional crystallization. There are exceptions in that some minerals concentrate REE, but these minerals tend to be relatively rare trace phases, with the exception of apatite that is a common minor phase in many rock types. Apatite and plagioclase prefer Nd over Sm ($D(\text{Nd}) > D(\text{Sm})$), but they are exceptions as most minerals fractionate Sm and Nd in the opposite sense. The most extreme in this sense is garnet, where the Sm partition coefficient is at least three times higher than for Nd, but can go even higher depending on the composition of the garnet (Table 2). For most other minerals, however, the difference between Sm and Nd partition coefficients is substantially less than a factor of two. The partition coefficients listed in Table 2 provide only an estimate of the values likely to operate in igneous differentiation as partition coefficients are functions of temperature, pressure, and the composition of both the mineral and melt. A particularly thorough discussion of partition coefficients and the crystal chemical parameters that determine them is given in Wood and Blundy (2003).

The similar partition coefficients for Sm and Nd in most minerals lead to relatively small variability in Sm/Nd ratio in most natural materials. For example, given the plagioclase and pyroxene partition coefficients listed in Table 2, a rock containing only plagioclase and pyroxene with a whole rock $^{147}\text{Sm}/^{144}\text{Nd} = 0.196$ (chondritic) will have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of 0.156 and 0.322 in the plagioclase and clinopyroxene, respectively. If the rock is 4.568 Ga old and today has a whole rock $^{143}\text{Nd}/^{144}\text{Nd} = 0.51263$ (chondritic), then, using Eq. 3, the rock formed with $^{143}\text{Nd}/^{144}\text{Nd} = 0.506686$. Today, the plagioclase and pyroxene have $^{143}\text{Nd}/^{144}\text{Nd} = 0.511417$ and 0.516451, respectively, a range of just under 1 % in isotopic composition. Using Eq. 5 with a modern-day whole rock $^{142}\text{Nd}/^{144}\text{Nd} = 1.141842$, solar system initial $^{146}\text{Sm}/^{144}\text{Sm} = 0.0094$ at 4.568 Ga, and $^{144}\text{Sm}/^{147}\text{Sm} = 0.20501$, the rock modeled above formed with $^{142}\text{Nd}/^{144}\text{Nd} = 1.1414573$. Today, the plagioclase and pyroxene have $^{142}\text{Nd}/^{144}\text{Nd} = 1.1417579$ and 1.1420778, respectively, a range of 0.028 %. If the rock instead formed at 1 Ga, then the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of its plagioclase and pyroxene would be 0.512368 and 0.513456, respectively, a range of 0.2 %. In a 1 Ga rock, the plagioclase, whole rock, and pyroxene would have essentially identical $^{142}\text{Nd}/^{144}\text{Nd}$ ratios because the rock formed when $^{146}\text{Sm}/^{144}\text{Sm} = 1.5 \times 10^{-18}$; hence, ^{146}Sm was, in essence, extinct at 1 Ga.

Sm and Nd also can be fractionated by partial melting. In the simple case where a source rock melts to a given degree (F) and the melt is then extracted from the remaining solid, the concentration of a trace element in the liquid (C_L) compared to its concentration in the starting solid (C_O) is given by the batch melting equation

$$C_L = C_O / (F + D - FD) \quad (6)$$

where D is the bulk distribution coefficient of the solid assemblage of minerals, which is calculated from the sum of the individual mineral distribution coefficients weighted by their modal abundance in the rock:

$$D = \sum X_M D_M \quad (7)$$

where D_M is the distribution coefficient for mineral “M” and X_M is the modal abundance of that mineral in the solid rock. For a typical fertile mantle peridotite composed of 60 % olivine, 20 % clinopyroxene, 10 % orthopyroxene, and 10 % garnet, the bulk D for Sm is 0.2 and for Nd is 0.093. Estimates of fertile mantle Sm and Nd concentrations are 0.406 and 1.25 ppm, respectively (McDonough and Sun 1995). Using equation 6, a 1 % melt of the mantle will have 1.92 ppm Sm and 12.2 ppm Nd for a $^{147}\text{Sm}/^{144}\text{Nd} = 0.095$. At 20 % melting, the melt will have 1.12 ppm Sm and 4.55 ppm Nd for a $^{147}\text{Sm}/^{144}\text{Nd} = 0.149$. Partial melting of the mantle thus will produce magmas with a fairly small range in Sm/Nd ratio that is always lower than the Sm/Nd ratio of the source rock. In contrast, because so much more Nd than Sm is partitioned into the melt during melting, the residue can develop quite high Sm/Nd ratios. In the 20 % melting case described above, the $^{147}\text{Sm}/^{144}\text{Nd}$ of the residue is 0.323. The fractionation of Sm from Nd during partial melting is the basis for perhaps the most significant use of Sm–Nd dating where variations in $^{143}\text{Nd}/^{144}\text{Nd}$ of igneous rocks are used to infer the time when their mantle source regions experienced some fractionation event that caused their composition to deviate from an estimate of the fertile mantle (see ► [Sm–Nd Model Ages](#)).

The examples above illustrate one of the weaknesses of the Sm–Nd dating system, the combination of small parent–daughter fractionation and the long half-life of ^{147}Sm conspire to create very limited variation in $^{143}\text{Nd}/^{144}\text{Nd}$. With typical modern measurement uncertainties of 0.1 % on Sm/Nd ratio and 20 ppm for $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, the igneous rock data modeled above produce an isochron with an age uncertainty of ± 13 Ma. For the $^{146}\text{Sm}/^{142}\text{Nd}$ system, where typical measurement precisions on $^{142}\text{Nd}/^{144}\text{Nd}$ are ± 5 ppm, the data above provide an age precise to ± 2 Ma. These age precisions are roughly an order of magnitude larger than the most precise ages currently being obtained with U–Pb in zircon (Schoene et al. 2006; Amelin 2008). Where Sm–Nd becomes important as a dating tool, however, is that not all rocks contain minerals with high enough U–Pb ratios to make them amenable for U–Pb dating. Examples include some types of meteorites, particularly those from Mars, most lunar rocks, and terrestrial Mg-rich rocks such as komatiites, basalts, layered mafic intrusions, and peridotites. In addition, garnet’s unique ability to strongly concentrate Sm over Nd, with $^{147}\text{Sm}/^{144}\text{Nd}$ ratios up to over 4 (Pollington and Baxter 2011), has turned garnet into a particularly useful mineral for Sm–Nd geochronology (see entry on ► [Sm–Nd, Metamorphic Rocks](#)).

The high isotope ratio precisions needed to provide useful chronological precisions were the primary factor that delayed the development of the Sm–Nd system as a geochronological tool. The first inroads into the use of Sm–Nd dating were two papers from the group at the University of Tokyo who reported ^{147}Sm – ^{143}Nd data for an eclogite inclusion in the Roberts Victor kimberlite of

South Africa (Notsu et al. 1973b) and both ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd data for the Juvinas eucritic meteorite (Notsu et al. 1973a). In both cases, the Nd isotopic composition for all phases measured was unresolved within the uncertainties of ~0.1–0.2 % (Fig. 2), but the work showed the potential of Sm–Nd dating if isotope ratio precisions could be improved. In 1975, Lugmair et al. (1975b) used ^{147}Sm – ^{143}Nd with Nd isotope ratio precisions of 80 ppm to determine an age of 3.70 ± 0.07 Ga for lunar mare basalt 75075. Perhaps more important, this work also started the use of the Nd model age approach to understand the time of chemical differentiation in the source region of a volcanic rock. Lugmair et al. (1975a) then attempted to find evidence of ^{146}Sm decay in the Juvinas meteorite (Fig. 2), but even with precision on $^{142}\text{Nd}/^{144}\text{Nd}$ improved to 60 ppm, they could not resolve variability in $^{142}\text{Nd}/^{144}\text{Nd}$ in the mineral separates. Convincing evidence for live ^{146}Sm in the early solar nebula had to wait until Lugmair and Marti (1977) improved the $^{142}\text{Nd}/^{144}\text{Nd}$ precision to 20 ppm and resolved variability in $^{142}\text{Nd}/^{144}\text{Nd}$ in mineral separates from the Angra dos Reis meteorite. With these precision improvements, the use, and diversity of uses, of the Sm–Nd dating system grew rapidly (DePaolo and Wasserburg 1976b; Lugmair et al. 1976; O’Nions et al. 1979; Allègre and Othman 1980; DePaolo 1980; Allègre et al. 1983; DePaolo 1988).

Sm–Nd Dating

While U–Pb dating of zircon (see ► [Zircon](#)) has reached a level of sophistication and precision in age determination for rocks that contain zircon that cannot be bettered by other dating systems, the Sm–Nd system has proven particularly useful for age dating of zircon-free rocks, which includes the majority of extraterrestrial rocks (see ► [Sm–Nd, Meteorites](#)) and Mg-rich rocks including basalts, komatiites, and peridotites. Sm–Nd dating has also been applied to date altered/metamorphosed rocks due to its greater stability through these processes compared to, for example, Rb–Sr and K–Ar dating (see ► [Sm–Nd Metamorphic Rocks](#)).

The Sm–Nd system has been heavily used in lunar geochronology because most lunar rocks do not contain zircon, and the Moon is highly depleted in volatile elements with the result that many lunar rocks have too low a concentration of volatile Rb to be amenable to precise Rb–Sr dating and such low concentrations of volatile Pb as to be extremely sensitive to contamination, thereby making U–Pb chronological measurements an analytical challenge. The first high-precision Sm–Nd age was determined on a lunar basalt (Lugmair et al. 1975b). An excellent summary of the application of Sm–Nd to understanding the history of lunar volcanism is given by Nyquist and Shih (1992). Sm–Nd chronology has been particularly important in defining the age range of the lunar highlands crust as most of the highlands crust consists of rocks highly dominated by plagioclase with variable amounts of pyroxene and/or olivine as their main mineral constituents. An example of a recent application of ^{146}Sm , ^{147}Sm – ^{142}Nd , and ^{143}Nd dating of what is perhaps the oldest lunar rock is found in Borg et al. (2011). For much the same reasons, Sm–Nd has been an essential dating tool for the Martian samples delivered to Earth as meteorites of the SNC – shergottite, nakhlite, and chassignite clan (Nyquist et al. 2001).

Another area where Sm–Nd dating has made a major contribution is in determining the timing of high-grade metamorphic events. This is enabled largely because of the extreme fractionation of Sm and Nd typical of garnet. For this reason, eclogites, the high-pressure form of basalt that is composed of pyroxene and garnet, are a common target for Sm–Nd dating (Mork et al. 1988; Chavagnac and Jahn 1996). As with all minerals, Sm and Nd diffuse through garnet at high temperature, but the diffusion is slow enough that garnet begins to faithfully maintain its record of Sm decay at temperatures below about 600 °C (Mezger et al. 1992), allowing garnet to serve as

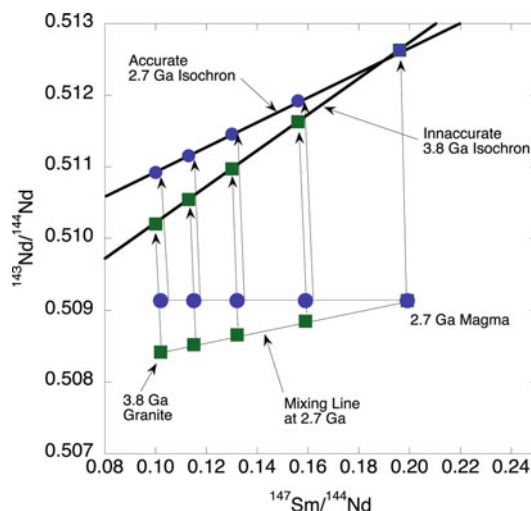


Fig. 3 Sm–Nd isochron diagram illustrating the potential and pitfall of whole rock isochrons. In this model, a magma is created by melting the mantle at 2.7 Ga. A portion of this magma undergoes crystal fractionation to create a series of compositionally distinct rocks with different Sm–Nd ratios, but, initially, the same $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (blue dots along horizontal line). After 2.7 billion years of evolution, these compositionally distinct rocks are measured today and give the blue points near the top of the figure that define a line whose slope gives an age of 2.7 Ga. The other example takes a portion of the 2.7 Ga magma and lets it mix, at 2.7 Ga, with a 3.8 Ga granite that has lower Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than the mantle-derived magma. This creates a group of mixed rocks shown by the green squares in the sloped line at the bottom of the graph. After 2.7 Ga of evolution, the rocks formed from the mixed magma create a steep-sloped line whose slope corresponds to 3.8 Ga, not 2.7 Ga

a useful thermochronometer for high-pressure metamorphism (Ducea et al. 2003; Pollington and Baxter 2010; see ► [Thermochronology, Tectonic Processes](#)).

Perhaps the most common application of Sm–Nd dating has been on ultramafic rocks on Earth as these generally have too low K, Rb, and U concentrations for dating by other methods. Good examples of this approach include layered mafic cumulate bodies such as the Stillwater (DePaolo and Wasserburg 1979), Muskox (Stewart and DePaolo 1992) and Great Dyke (Mukasa et al. 1998), ophiolites (Jacobsen and Wasserburg 1979; McCulloch et al. 1981; Shaw et al. 1987; Li et al. 1997), and particularly komatiites (Hamilton et al. 1977; Jahn et al. 1982; Machado et al. 1986; Puchtel et al. 2009).

The use of Sm–Nd dating to determine the age of komatiites opens the discussion of the benefits/risks of isochrons constructed from compositionally distinct whole rocks as opposed to isochrons created by separating the constituent minerals from a single rock. In most cases, komatiite Sm–Nd ages involve whole rock isochrons. There are two reasons for turning to whole rock isochrons. First, many old mafic/ultramafic rocks have been subjected to sufficient alteration/metamorphism that little of their original igneous mineralogy remains. In the case of komatiites, the original pyroxenes and olivines often have been transformed into amphiboles and serpentines by the addition of water during metamorphic reactions upon their burial in the deep crust. In these cases, the Sm–Nd ratios of the metamorphic minerals will not be the same as the original igneous minerals and hence will not define an isochron that gives the igneous age of the rock. Second, heating of minerals causes their constituent elements to move, diffuse, through the crystal lattice. Burial of rocks in the deep crust can raise their temperature by hundreds of degrees. At these temperatures, fast-diffusing elements can move millimeter distances over billions of years. The diffusional movement will serve to mix the Nd in nearby minerals, erasing, or lessening, the Nd isotopic difference caused by the decay of ^{147}Sm in the minerals due to their different Sm/Nd ratios.

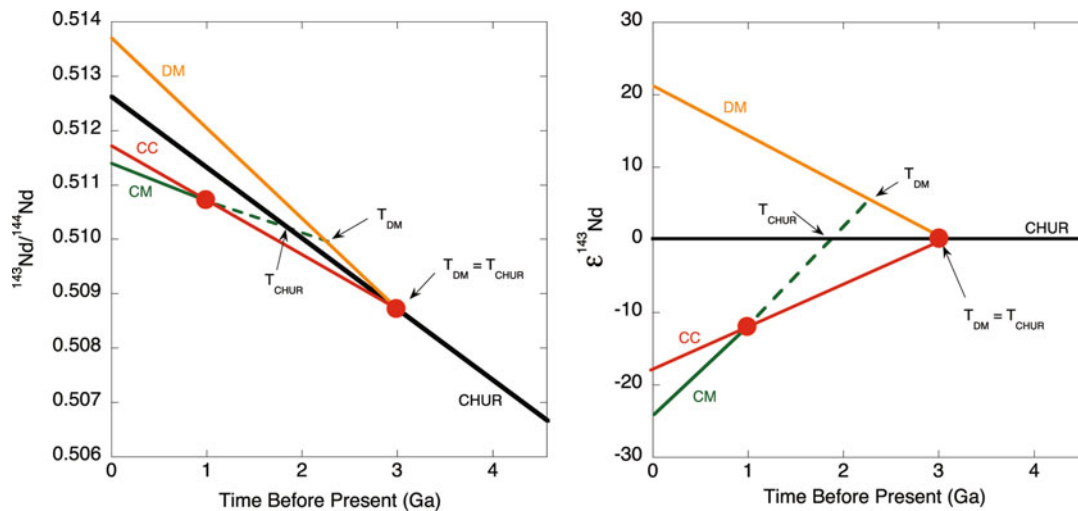


Fig. 4 Model time evolution in $^{143}\text{Nd}/^{144}\text{Nd}$ (left) and transformed to $\epsilon^{143}\text{Nd}$ (right). The thick black line in each plot shows the ingrowth of ^{143}Nd in a material that has chondritic Sm/Nd ratio (CHUR). In this example, a melting event takes place at 3 Ga that creates a melt with low Sm/Nd ratio (CC) and a residue (DM) with high Sm/Nd ratio. The different Sm/Nd ratios of the two rocks formed in this event cause their $^{143}\text{Nd}/^{144}\text{Nd}$ to diverge from the CHUR line. Measuring the $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd ratio of the samples of CC and DM today allows reconstruction of their Nd isotope evolution lines back in time. The slope of the isotope evolution line is proportional to Sm/Nd ratio. The intersection of these lines with the CHUR evolution line defines the chondritic model age (T_{CHUR}). In this model, a second melting event occurs to CC at 1 Ga to create a new rock with lower Sm/Nd ratio (CM). Measuring the Sm/Nd ratio and $^{143}\text{Nd}/^{144}\text{Nd}$ of this sample today allows the calculation of the green line. The extrapolation of this line to the CHUR and DM evolution lines provides two different model ages. In this case, both are substantially older than the 1 Ga melting event and show that CM was derived by reworking/remelting of CC, not as a new melt from the material evolving with either CHUR or DM Sm/Nd ratio

By moving to the many centimeter-size hand-sample scale of whole rocks, the consequences of this diffusional resetting of the Sm–Nd clock will be minimized.

Equation 3, however, requires that all the samples used to define an isochron must have started with the same initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in order for that line to provide an accurate age. While the expectation that all minerals crystallizing from a magma will inherit the same $^{143}\text{Nd}/^{144}\text{Nd}$ from the magma usually, but not always (Prevec et al. 2005), is met, the limited Sm–Nd fractionation during partial melting and fractional crystallization often requires including a wide range of rock compositions on a Sm–Nd whole rock isochron in order to obtain enough spread in Sm/Nd ratio to define a precise isochron. If all the rocks used to construct the isochron indeed started with the same initial $^{143}\text{Nd}/^{144}\text{Nd}$, and formed at the same time, then the whole rock isochron will give the correct age (Fig. 3).

Magmas moving from source to eruption, however, often interact with the surrounding rock. If the surrounding rock is isotopically distinct from the magma, then mixing between the two can create hybrid magmas that have isotopic compositions between the two end-members as shown in Fig. 3. Allowing these mixtures to evolve through ^{147}Sm decay with their different Sm–Nd and initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios to the present day will produce a linear array of data that gives a meaningless age somewhere between the age of magmatism and that of the wall rock contaminant. This problem was first highlighted when whole rock Sm–Nd dating of komatiites from Kambalda, Australia, gave an age 500 Ma older than their stratigraphic age constrained by U–Pb geochronology of over- and underlying rock strata (Chauvel et al. 1985). Although presenting a major obstacle for Sm–Nd whole rock dating, using Sm–Nd systematics to detect and understand

the process of crustal contamination has been an important application of the Sm–Nd system in rocks where the age can be constrained by other means (Carlson et al. 1981; DePaolo 1981; Stewart and DePaolo 1992; Lambert et al. 1994).

Sm–Nd Tracing of Geologic Processes

Because the processes that most strongly fractionate Sm from Nd are partial melting and crystal fractionation, the Sm–Nd system is particularly useful for determining the time at which a rock, or its source materials, had its Sm/Nd ratio changed from that of some model for mantle Nd isotope evolution. Figure 4 shows an example of how Nd isotope measurements can be used to understand the source history of igneous rocks. In this model, the $^{143}\text{Nd}/^{144}\text{Nd}$ of the mantle is evolving with a Sm/Nd ratio equal to chondritic, often called the “chondritic uniform reservoir,” or CHUR. If a portion of CHUR melts to produce a melt and residue, the different Sm/Nd ratios of these complementary components cause their Nd isotope evolution to diverge from the CHUR Nd isotope evolution line. If nothing else happens to either melt or residue, the age of this differentiation event can be calculated from the measured $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd ratios of either melt or residue using the equation

$$T_{\text{CHUR}} = 1/\lambda \times \ln \left(\left(^{143}\text{Nd}/^{144}\text{Nd} \right)_{\text{M}} - \left(^{143}\text{Nd}/^{144}\text{Nd} \right)_{\text{CHUR}} \right) / \left(\left(^{147}\text{Sm}/^{144}\text{Nd} \right)_{\text{M}} - \left(^{147}\text{Sm}/^{144}\text{Nd} \right)_{\text{CHUR}} \right)$$

where “M” stands for the measured values. While the model age approach is straightforward mathematically, interpretation of the age obtained depends on the number of differentiation steps involved in producing any given rock sample and particularly on the Nd isotope evolution path chosen for the model primitive reservoir. Early applications of Sm–Nd model ages usually referred to a primitive mantle evolution characterized by a chondritic Sm/Nd ratio. As Nd data became more abundant, mantle-derived rocks through time defined a mantle evolution characterized by higher than chondritic $^{143}\text{Nd}/^{144}\text{Nd}$ (Shirey and Hanson 1986). Interpretations of this result ranged from assuming that the Sm/Nd ratio of the mantle had been raised due to extraction of the low Sm/Nd ratio continental crust (DePaolo et al. 1991) to the possibility that the mantle never had a chondritic Sm/Nd ratio (Boyet and Carlson 2005). Whichever explanation is correct, Nd model ages now are mostly calculated relative to a “depleted mantle” instead of CHUR evolution. There is some variability in the values used for the Sm/Nd evolution parameters in calculating depleted mantle model ages, but a good compromise, and a well reasoned argument for the choice of values, is that presented by DePaolo et al. (1991). These authors suggest replacing $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}$ with $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{DM}} = 0.51307$ and $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}$ with $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{DM}} = 0.2105$ for calculating Nd model ages using equation 8 where “DM” is depleted mantle. While uncertainties of this nature in the Nd evolution of the “model” in Sm–Nd model age dating have a significant effect on the ages calculated, they do not detract from the usefulness of such “mantle separation ages” in helping to distinguish whether a given rock was newly added to the continental crust via melting of the mantle or instead reflects reworking/remelting of older crust (see entry on ► [Sm–Nd Model Ages](#)). This type of information has been particularly useful in constructing maps showing crustal age terranes that define the borders of new crustal additions.

Conclusion

Forty years of application of the Sm–Nd dating system has established it as a crucial component in the geochronology/geochemistry toolbox. While hard-pressed to provide dating precision comparable to techniques such as U–Pb in zircon, the Sm–Nd systems can be applied widely across a variety of rock types. This characteristic has led it to be used extensively in dating mafic and ultramafic rocks, be they from Earth or elsewhere. In addition, Sm–Nd has become a useful chronometer for high-pressure and high-temperature metamorphic events. Among its many uses, perhaps the most common is its ability to illuminate the history of crust–mantle differentiation through model age approaches that follow rocks from an early origin in a hypothetical undifferentiated bulk planet to the differentiated crusts and mantles that we find on Earth, Moon, Mars, and asteroids today.

Cross-References

- ▶ [Extinct Radionuclide Dating](#)
- ▶ [Samarium–Neodymium, Igneous Rocks](#)
- ▶ [Samarium–Neodymium Metamorphic Rocks](#)
- ▶ [Samarium–Neodymium Meteorites](#)
- ▶ [Samarium–Neodymium, Model Ages](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [Thermochronology, Tectonic Processes](#)
- ▶ [Zircon](#)

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Rhenium–Osmium Dating (Meteorites)

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Synonyms

¹⁸⁷Re–¹⁸⁷Os isotopic dating; Osmium isotopic dating

Definition

The Re–Os isotopic system is used for determining formation ages and constraining ages of secondary alteration of meteorites and meteorite components, especially in relation to metals and sulfides.

Introduction

The rhenium-osmium isotopic dating system as applied to geo- and cosmochemical materials is based on the negatron (β^-) transition of ¹⁸⁷Re to ¹⁸⁷Os. The decay constant (λ) for ¹⁸⁷Re is $1.67 \times 10^{-11} \text{ year}^{-1}$, which is equivalent to a half-life ($t_{1/2}$) of approximately 42 billion years. This value has been determined through the comparisons of precisely defined isochrons for cosmochemical and terrestrial materials to absolute ages for the same materials determined using the U–Pb system (Smoliar et al. 1996; Selby et al. 2007). The Re–Os isotopic system has been of interest to the cosmochemical community for more than 50 years because of the unique geochemical characteristics of both elements, as compared to elements comprising other long-lived chronometers. Both elements partition nearly quantitatively into metal relative to silicates; hence, they are termed highly siderophile elements (HSE). In addition, both elements also tend to strongly partition into sulfides and sulfide melts relative to silicates; hence, they are also chalcophile elements. Consequently, the system has been long pursued as a means of determining the ages of early solar system metals, such as iron meteorites, and the metal and sulfide components of some primitive meteorites. Because of the relatively high abundances of Re and Os in primitive and iron meteorites, and their relatively low abundances in the silicate mantles and crusts of differentiated planetary bodies, the system can also potentially serve as a tracer of the chemical natures and quantities of late accreted materials to planetary bodies (Chou 1978; Morgan 1986; Morgan et al. 2001).

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Historical Development of System to Dating Meteorites

Early studies of the Re–Os system, as applied to both geo- and cosmochemical problems, were hindered by extreme analytical limitations. These limitations mainly stemmed from the very high first ionization potentials of Re and Os, resulting in extremely low thermal ionization yields, when using the standard thermal ionization mass spectrometric methods available in the 1950s–1980s. Despite the analytical limitations, the first detailed application of the Re–Os isotopic system to dating meteorites was published by Hirt et al. (1963). In that study the authors examined variations in $^{187}\text{Os}/^{186}\text{Os}$ and $^{187}\text{Re}/^{186}\text{Os}$ for a variety of iron meteorites. The low-precision data were found to form a linear trend that was interpreted to be an isochron. The generation of isochrons in this and subsequent studies of iron meteorites were advantaged by the large range of Re–Os ratios typically present within iron meteorite groups. Most such variations are consistent with solid metal–liquid metal fractionation on the parent bodies of the meteorites (e.g., McCoy et al. 2011). Hirt et al. (1963) applied a ^{187}Re half-life of 43 billion years to their iron meteorite isochron and suggested a general crystallization age for irons of approximately 4.0 billion years. Subsequent studies of the Re–Os isotopic systematics of iron meteorites and metal components from chondritic meteorites were published by Luck et al. (1980) and Luck and Allègre (1983). These studies, which utilized secondary ion mass spectrometry of the chemically purified elements, reported much higher precision isotopic and elemental compositions, compared to the prior studies. They also reported good linear trends for meteorites on plots of $^{187}\text{Re}/^{186}\text{Os}$ versus $^{187}\text{Os}/^{186}\text{Os}$, interpreted the correlations to be isochrons, and redefined the decay constant for ^{187}Re so that the isochrons would give ages close to the 4.57 Ga canonical age of the solar system. Regression uncertainties for isochrons slopes in these studies, however, were no better than $\pm 2\%$, equivalent to uncertainties of ± 90 million years for early solar system objects.

Analyses of bulk chondrites, as well as metal separates from chondrites, were found to be characterized by limited variations in Re–Os and $^{187}\text{Os}/^{186}\text{Os}$, compared to iron meteorites (Luck and Allègre 1983; Walker and Morgan 1989), so the generation of precise isochrons for these types of materials was not possible. Further, analyses of some bulk chondrites, determined by resonance ionization mass spectrometry, did not plot within analytical uncertainties of the iron meteorite reference isochron, indicating either incorporation of isotopically diverse Os into primitive meteorites at the time of formation or relatively late-stage open-system behavior (Walker and Morgan 1989).

Iron Meteorites

The development of negative thermal ionization mass spectrometry (NTIMS) techniques in the early 1990s, as applied to the Re–Os system, permitted the measurement of these elements to much higher precision than was previously possible (Creaser et al. 1991; Völkening et al. 1991). Also, at about this time, the common reference isotope for Os was changed from ^{186}Os to ^{188}Os , because of the recognition that ^{186}Os is the decay product of ^{190}Pt and that its atomic abundance, relative to the non-radiogenic isotopes of Os, varies in nature. Coupled with improved chemical processing methods (Shirey and Walker 1995), the NTIMS technique permitted the generation of high-precision isochrons for iron meteorite groups representing five different parent bodies (e.g., Horan et al. 1992; Shen et al. 1996; Smoliar et al. 1996; Cook et al. 2004; Walker et al. 2008; McCoy et al. 2011). For example, Smoliar et al. (1996) reported an isochron age for group IIAB irons of $4,537 \pm 8$ Ma, with a precision of better than $\pm 0.2\%$. Isochron ages with nearly

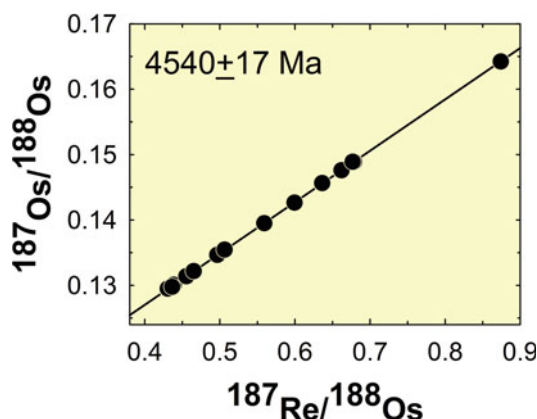


Fig. 1 Isochron diagram for group IVA iron meteorites. Meteorites from this group display a relatively large range in $^{187}\text{Re}/^{188}\text{Os}$ and corresponding $^{187}\text{Os}/^{188}\text{Os}$. The crystallization age derived from this isochron is $4,540 \pm 17$ Ma (Figure is from McCoy et al. (2011))

comparable precision have been reported for other major iron meteorite groups (IAB, IIIAB, IVA, and IVB), constraining the ages of crystallization to the first 50 Ma of solar system history (Fig. 1). Unfortunately, crystallization ages with uncertainties of 10–20 million years are of limited utility with regard to understanding the chronological sequence of planetesimal formation, melting, differentiation, and crystallization, given that many such bodies evidently underwent some or all of these processes within the first 10 million years of solar system history (e.g., Lugmair and Galer 1992; Misawa et al. 2005; Day et al. 2012b). Application of the short-lived ^{182}Hf – ^{182}W isotopic system ($t_{1/2}$ of ^{182}Hf is 8.9 million years) has revealed that, in most cases, metallic cores *segregated* from silicates within just the first ~3 million years of solar system history (e.g., Horan et al. 1998; Kruijer et al. 2012). It should be noted, however, that ^{182}W model ages of iron meteorites define the timing of metal-silicate segregation, not crystallization. Hence, the Re–Os system retains utility for understanding the cooling rates of cores of larger, more slowly cooled bodies. Further, the system has been used to examine whether or not the HSE within a given iron meteorite have remained closed to elemental migration, due to impact resetting or other processes, since the time of formation (e.g., McCoy et al. 2011).

Primitive Meteorites

The application of the Re–Os system to dating bulk chondritic meteorites and their components has met with mixed success. Even with improved analytical methods, most bulk samples of chondrites from the major groups do not define sufficient spread in Re–Os to permit the generation of precisely defined group isochrons, even assuming that the requirements for isochron dating of different primitive meteorites could be met (same formation ages; derived from isotopically uniform sources). Hence, the system has virtually no utility for dating the formation of primitive meteorites. Further, a major proportion of bulk chondrites analyzed using NTIMS do not plot within analytical uncertainties of a primordial reference isochron (Chen et al. 1998; Walker et al. 2002; Fischer-Gödde et al. 2010; van Acken et al. 2011) (Fig. 2a). Such deviations have largely been interpreted to reflect open-system behavior tens of millions of years to billions of years after the parent bodies formed. Open-system behavior on primitive parent bodies may reflect late-stage impact heating and/or aqueous alteration.

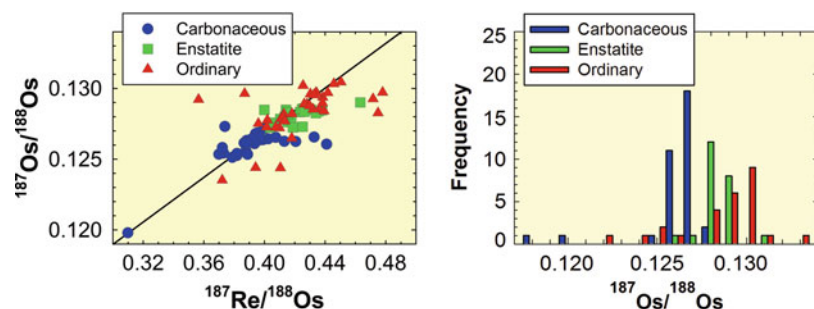


Fig. 2 (a) Isochron diagram for primitive (chondritic) meteorites. Bulk samples of chondrites from the carbonaceous, enstatite, and ordinary chondrite groups are characterized by limited variations in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$, compared to most within-group variations for iron meteorites (e.g., Fig. 1 above). Analytical uncertainties are typically smaller than the symbols. The considerable variance of data around the 4.57 Ga reference isochrons reflects relatively late-stage open-system behavior of Re and/or Os. (b) Histogram showing the distributions of $^{187}\text{Os}/^{188}\text{Os}$ in the three major groups of chondrites (Data are from Walker et al. (2002), Fischer-Gödde et al. (2010), and van Acken et al. (2011))

As the nature and intensity of open-system behavior appears to be mostly specific to individual meteorites, not chondritic groups or subgroups (Walker et al. 2002), the study of components from a meteorite is a potentially important means for investigating the processes involved in creating the open-system behavior specific to the sampled portion of the parent body. Common components present in primitive meteorites include chondrules, calcium-aluminum-rich inclusions (CAIs), and matrix. As with bulk chondrites, several studies have documented open-system behavior among chondritic components from the same meteorites. For example, Becker et al. (2001) analyzed CAIs from the carbonaceous chondrite Allende and found moderate-scale open-system behavior. Analyses of multiple pieces of a single CAI were characterized by sufficient spread in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ to define an errorchron that defined a reset age of $\sim 1,600$ Ma. Presumably a metamorphic event led to the isotopic homogenization of Os within the CAI at that time. Horan et al. (2009) reported large variations in $^{187}\text{Re}/^{188}\text{Os}$, and consequently $^{187}\text{Os}/^{188}\text{Os}$, between magnetic and nonmagnetic portions of chondrules and matrix separated from the relatively low metamorphic grade ordinary chondrites Dhajala and Ochansk. In contrast to the Allende CAIs, they reported relatively minor open-system behavior for these components. Collectively, these studies show that the Re–Os system will continue to play an important role in constraining the timing of late-stage events affecting primitive meteorites.

Perhaps the greatest utility of the Re–Os isotopic system, as applied to primitive meteorites, is for genetic tracing. On average, carbonaceous chondrites have less radiogenic $^{187}\text{Os}/^{188}\text{Os}$ than ordinary or enstatite chondrites (Fig. 2b). This reflects the lower long-term $^{187}\text{Re}/^{188}\text{Os}$ of carbonaceous chondrites, which, in turn, may reflect a nebular fractionation compared with the formational environments of enstatite and ordinary chondrites. The lower $^{187}\text{Os}/^{188}\text{Os}$ of carbonaceous chondrites has been useful, for example, in assessing their role (or lack thereof) in the generation of terrestrial and lunar impact melt rocks (e.g., Puchtel et al. 2008; Fischer-Gödde and Becker 2012).

Achondrite Meteorites

Rhenium–Os isotopic data have been published for a number of types of achondritic meteorites including the shergottite-nahklite-chassignite (SNC) suite, presumed to be derived from Mars

(Birck and Allègre 1994; Brandon et al. 2012); the howardite-eucrite-diogenite (HED) suite, presumed to be derived from the asteroid Vesta (Dale et al. 2012; Day et al. 2012b); as well as angrites and ureilites (Rankenburg et al. 2007; Riches et al. 2012). The system has also been examined in various primitive achondrites, such as brachinites (Day et al. 2012a), as well as lunar meteorites (Puchtel et al. 2008). Given the inherent problems relating different meteorites to one another through a common process and formation time, the system has proved useful from a geochronologic standpoint only for dating individual meteorites from which bulk pieces or separated minerals define substantial variation in Re–Os. Consequently, the Re–Os isotopic system has been only sparingly applied to dating achondrites. For example, Brandon et al. (2012) reported a Re–Os isochron age of 164 ± 12 Ma for the Antarctic shergottite EETA 79001. This age is in good agreement with Sm–Nd and Rb–Sr isochrons ages for the same meteorite and provides important supporting evidence that relatively young ages for some shergottites are true igneous crystallization ages, rather than reset ages associated with impact events.

Most Re–Os data as well as accompanying concentration data for other HSE in achondrites have been used to consider the origins of HSE to the silicate portions of the parent bodies to these meteorites. For example, Day et al. (2012b) concluded that diogenites were variably enriched in the HSE via a process termed late accretion, whereby additional meteoritic material accreted to the parent body after cessation of core segregation, leading to a re-enrichment of HSE in the silicate portion of the body (Walker 2009). Evidence for variable extents of late accretion is present in the terrestrial mantle (Meisel et al. 2001; Becker et al. 2006), the lunar mantle (Day et al. 2007), and the Martian mantle (Brandon et al. 2012).

Summary and Conclusions

Since the 1960s the Re–Os isotopic system has been used for dating various cosmochemical materials. The system has primarily been applied to constraining crystallization ages of large metal masses, such as asteroidal cores, via the analysis of chemically related iron meteorites. However, due to the limited precision of isochron ages for irons, the system has proved more important for demonstrating long-term closed-system behavior for the HSE in those metals studied. The system has little utility for precisely dating the absolute formation ages of bulk chondrites and their components, but is quite valuable for constraining periods of open-system behavior in chondritic components, such as CAIs and chondrules.

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Crustal Sulfide Minerals (Re-Os)

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Definition

The rhenium-osmium (^{187}Re - ^{187}Os) radioactive isotope system can be used to determine absolute age dates for some sulfide minerals formed in a variety of crustal geologic environments, including those associated with igneous, sedimentary, and metamorphic processes. Sulfide minerals that have yielded reliable Re-Os age dates include molybdenite (MoS_2), pyrite (FeS_2), and arsenopyrite (FeAsS), although many other sulfide minerals have potential for yielding Re-Os age dates. This entry deals with Re-Os geochronology of crustal sulfide minerals typically formed from aqueous fluids, either hydrothermal or diagenetic, and does not consider orthomagmatic sulfide minerals.

Introduction

Following the discovery of the natural radioactivity of ^{187}Re by negatron decay (Naldrett and Libby 1948), some of the earliest applications of ^{187}Re - ^{187}Os geochronology involved the crustal sulfide mineral molybdenite (MoS_2 – Hirt et al. 1963; Luck and Allègre 1982). During these early years, the analytical methods available were such that only molybdenite, a mineral that contains parts-per-million (ppm) level Re abundances, was realistically the sole crustal sulfide mineral amenable for Re-Os isotopic analysis. Following major analytical breakthroughs in mass spectrometry (Creaser et al. 1991; Volkening et al. 1991), sample digestion, and spike-sample equilibration methods (Shirey and Walker 1995; Cohen and Waters 1996; Birck et al. 1997), other crustal sulfide minerals such as pyrite, typically containing parts-per-billion (ppb) level of Re and parts-per-trillion (ppt) level of Os, became amenable for isotopic analysis, with potential application as geochronometers. Given the widespread geological occurrence of crustal sulfide minerals such as pyrite, development and application of the Re-Os method for these minerals is an important recent development in isotopic dating, particularly for research areas such as ore deposit geology, in which the mineralogy can be dominated by sulfide minerals and for which obtaining accurate and precise ages dates for mineral formation can be problematic (Richards and Noble 1998).

Methodology: Analytical Protocol

The majority of modern analyses for Re-Os in crustal sulfide minerals involve mineral separation and purification, spiking with isotopically enriched tracer solution(s) and chemical digestion in inverse *aqua regia* using Carius tube methodology (Shirey and Walker 1995). Chemical purification of Re and Os typically uses organic solvent extraction, ion-exchange, and microdistillation

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methods (Cohen and Waters 1996; Birck et al. 1997) and is followed by isotope dilution negative thermal ionization mass spectrometry for isotopic analysis of both Os and Re (NTIMS – Creaser et al. 1991; Volkening et al. 1991). Sample preparation – crushing and milling of rock to purify sulfide minerals – uses nonferrous materials such as ceramic and agate, to avoid contamination by Re and Os present in steel. The choice of isotopically enriched tracer depends on the nature of Os present in the sulfide mineral. For example, molybdenite rarely contains measurable “common Os” – Os incorporated at the time of formation – and consists entirely of radiogenic ^{187}Os . In this case, a “double spike” of $^{188}\text{Os} + ^{190}\text{Os}$ is preferred, combined with ^{185}Re (e.g., Markey et al. 2003) to permit accurate mass bias correction during isotopic analysis and to monitor possible common Os in the sample. In some cases, crustal sulfide minerals such as arsenopyrite also contain little or no common Os (Morelli et al. 2005), and the “mixed double-spike” method is also used. In these cases, uncertainties in the quantification of ^{188}Os can be large, as it is dominated by blank ^{188}Os , so uncertainties in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ are highly correlated on a traditional isochron plot. In this case, the correlation coefficient ρ must be used for isochron regression analysis (Morelli et al. 2005) or a modified plot used that eliminates ^{188}Os (Stein et al. 2000). Many crustal sulfide minerals like pyrite typically do contain trace amounts of common Os, and a mixed $^{185}\text{Re} + ^{190}\text{Os}$ spike is typically used for quantification of Os and Re abundances in these cases. Re and Os abundances can be very low in many cases (Ootes et al. 2011), and laboratory blank levels for Re and Os must be extremely low (<1 pg) and monitored for blank $^{187}\text{Os}/^{188}\text{Os}$ value. Age quantification for samples with no common Os uses the simplified equation:

$$t = \ln \left(^{187}\text{Os}/^{187}\text{Re} + 1 \right) / \lambda$$

from which a single age is calculated based on the measured ^{187}Re and ^{187}Os abundances, whereas for samples with common Os, the isochron approach using multiple co-genetic samples is applied. The value of the ^{187}Re decay constant (λ) of $1.666\text{e}^{-11} \cdot \text{a}^{-1}$ (Smoliar et al. 1996) is used. Although a relatively new method, Re-Os geochronology of crustal sulfide minerals has progressed to the point of establishing reference age materials for inter-laboratory comparison (Markey et al. 2007).

Re-Os Geochronology of Molybdenite

Molybdenite (MoS_2) is ideal for geochronology using the ^{187}Re - ^{187}Os isotope system, as it is enriched in Re and is usually devoid of common Os, so nearly all ^{187}Os is radiogenic, derived from the decay of ^{187}Re . Although some early studies concluded Re-Os age dating of molybdenite to be inaccurate or easily disturbed (Luck and Allègre 1982; McCandless et al. 1993; Suzuki et al. 2001), Stein et al. (2001) found that this likely relates to internal spatial decoupling of radiogenic ^{187}Os from Re within molybdenite grains and that accurate age dates could be obtained if sufficiently large sample sizes were analyzed. Investigation of Re-Os in molybdenite at the micron scale using laser ablation ICP-MS methods confirmed these findings, by producing highly inaccurate ages of very small sampled volumes (Stein et al. 2003; Kosler et al. 2003; Selby and Creaser 2004). Since this limitation was discovered and suitable analysis methods adopted, the Re-Os geochronometer in molybdenite has proven to be highly robust, showing excellent cross-calibration to U-Pb zircon ages for igneous-associated molybdenite deposits back to Archean time (Selby et al. 2007). Bingen and Stein (2003) found that the Re-Os system in molybdenite has a thermal resetting temperature (closure or blocking temperature) well above 800 °C. Molybdenite Re-Os geochronology has developed into an invaluable dating method in metallic ore deposit research, as it is a common

accessory mineral in porphyry Cu-(Mo-Au) deposits, pegmatite and rare metal deposits, iron oxide-Cu-Au-U (IOCG-type) deposits, and intrusion-related Au deposits. It provides direct age control for the formation of sulfide minerals in a variety of ore-forming systems to evaluate the general tectonomagmatic affinity of ores (Chiaradia et al. 2009; Mao et al. 2003), to test the igneous affiliation of ores (Reid et al. 2013; Selby et al. 2002), and to investigate the temporal connections between mineralization and volcanism (Rosera et al. 2013). The precision of Re-Os molybdenite ages is typically $\sim 0.4\%$ (2σ , e.g., Stein et al. 2001), equating to age uncertainties of ± 5 to 10 Ma in Archean time for individual molybdenite age dates and thus not comparable to the precision attained by U-Pb dating of minerals like zircon (e.g., Piercey et al. 2008). However, in geologically young ore systems, Re-Os age dates of molybdenite can have age precision of < 50 Ka, providing temporal control within the history large mineralized intrusive complexes (e.g., Deckart et al. 2013). Although rare, multiple age components have been described within molybdenite crystals (Aleinikoff et al. 2012). Molybdenite paragenesis is mostly related to hydrothermal ore deposition, but it has also been found to form under high-grade metamorphic conditions associated with partial melting reactions and leucosome formation (Stein 2006).

Re-Os Geochronology of Pyrite and Arsenopyrite

Following the major advancements in the analysis of Re-Os isotopes made in the 1990s, analysis of crustal sulfide minerals other than molybdenite became feasible, with several early papers investigating Re-Os geochronology of pyrite (Stein et al. 1998; Mathur et al. 1999; Stein et al. 2000; Arne et al. 2001). These studies found Re levels in pyrite ranging up to a few tens of ppb, in some cases with little common Os present (Stein et al. 2000) enabling direct Re-Os age dating of a very common ore sulfide mineral in massive sulfide and gold vein deposits. Since then, the Re-Os geochronometer in pyrite has been used widely in ore deposit research to date the timing of vein versus massive ore formation in sedimentary exhalative-type deposits (SedEx; Morelli et al. 2004), to connect orogenic gold deposits with deep crustal metamorphism (Ootes et al. 2011), and to link polymetallic deposits to magmatism (Zhu et al. 2013). In terms of thermal resetting, Brennan et al. (2000) found that Os diffusion in pyrite is very slow, leading to estimates of 500°C for 10 Ma to affect the cores of 500 μm pyrite crystals, and Morelli and Creaser (2007) studied metamorphosed sulfide ores to estimate Re-Os resetting temperatures above 600°C for pyrite. Beyond ore deposit research, synsedimentary to early diagenetic pyrite from carbonaceous shales has been used to provide age constraints within Proterozoic sedimentary basins (Hannah et al. 2004).

Arsenopyrite (FeAsS) is typically restricted to hydrothermal vein and contact metamorphism occurrences, but As is an important pathfinder element for gold ores (Nude et al. 2012) as arsenopyrite is a host for many refractory gold deposits. Thus, the ability to precisely date arsenopyrite with Re-Os is an invaluable tool for gold deposit research. This was first reported by Arne et al. (2001) who used the method to confirm an Ordovician age for the historical Bendigo gold reefs in Australia. Arne et al. (2001) found arsenopyrite to have Re contents above 10 ppb, with little common Os and high Re/Os ratios, thus ideal for geochronology. Morelli et al. (2005) presented a detailed study of arsenopyrite geochronology from the Meguma terrane, Canada, where they identified two distinct ages of mineralization at ~ 380 Ma and 408 Ma. Within the deposits studied, some arsenopyrite contained no common Os, and the ages determined from those samples using the “mixed double-spike” approach were identical to other samples from which the age was determined using the conventional isochron approach. The Re-Os method in arsenopyrite has been used to establish the age of giant gold ore deposits worldwide (Yu et al. 2005; Morelli et al. 2007;

Morelli et al. 2010) and to evaluate models for their origin. An important cross-calibration to the U-Pb zircon geochronometer was presented by Scherstén et al. (2012) who reported Re-Os ages from arsenopyrite of $2,636 \pm 23$ Ma and U-Pb ages from metamorphic zircon of $2,633 \pm 6$ Ma, both of which formed during the same episode of metamorphism at that time. This implies that the closure temperature for Re-Os in arsenopyrite is, like molybdenite, high and well above 500°C (e.g., Morelli et al. 2010). Davies et al. (2010) found that Re-Os ages recorded by arsenopyrite ($1,768 \pm 11$ Ma) overlaps with U-Pb ages recorded by monazite ($1,781 \pm 4$ Ma) in a metamorphosed Proterozoic gold deposit, again implying a high closure temperature for Re-Os in arsenopyrite ($>600^\circ\text{C}$) that is demonstrably higher than the Ar-Ar mica closure temperature ($\sim 350^\circ\text{C}$) which records cooling ages of ca. 1,720 Ma from the deposit studied.

Re-Os Geochronology of Other Crustal Sulfide Minerals

Several copper sulfide minerals including chalcopyrite (CuFeS_2) and bornite (Cu_5FeS_4) have been investigated for Re-Os geochronology. A detailed study by Selby et al. (2009) found extremely high Re contents in both minerals up to 5,000 ppb, with little common Os, in sediment-hosted Cu deposits from Alaska, and bornite, chalcopyrite, and pyrite yielded a precise Re-Os age that resolved possible origin models for the deposit. Extremely high Re contents also characterized bornite and chalcopyrite from sandstone-hosted Cu deposits of Dzhezkazgan, Kazakhstan (Box et al. 2013). In this study, bornite and chalcopyrite yielded similar ages from one deposit but disparate ages from another. Zhu and Sun (2013) used Re-Os geochronology of chalcopyrite to provide the age of formation of IOCG deposits from China and again found Re levels above 1,000 ppb and low common Os contents. Thus, the copper sulfide minerals hold significant promise for Re-Os geochronology, and both Selby et al. (2009) and Zhu and Sun (2013) report retention of Re-Os ages in these minerals despite low-grade metamorphic overprints for each deposit.

Hydrothermal pyrrhotite ($\text{Fe}(1-x)\text{S}_x$) was analyzed by Morelli et al. (2010) from the Homestake Au deposit, from which a precise 1,736 Ma Re-Os arsenopyrite age was produced. In comparison to arsenopyrite, the pyrrhotite Re-Os data were highly scattered and did not yield useful age information. Brenan et al. (2000) measured Os diffusion in pyrrhotite and found it to be much faster than pyrite, yielding a likely closure temperature for pyrrhotite of $300\text{--}400^\circ\text{C}$. The Re-Os pyrrhotite results of Morelli et al. (2010) fit broadly with these experimental findings. Similarly, sphalerite (ZnS) was found to yield scattered Re-Os data from veins studied by Morelli et al. (2004) from which pyrite yielded a precise Re-Os age.

Few minerals contain Re as major component of their structure, but reeniite (ReS_2) has been reported in modern volcanic centers and remarkably has yielded isotopic Re-Os ages as young as 79 ± 11 a (Tessalina et al. 2008).

Summary

The common occurrence of sulfide minerals in metallic ore deposits (e.g., those of Cu, Au, Zn, and Pb) makes Re-Os dating of these minerals a key method in ore deposit research, particularly given the difficulty of directly dating ore minerals with other isotopic methods. It is relatively a new field of geochronology, enabled by significant advancements in analysis methods, that is becoming widely applied. Many crustal sulfide minerals (molybdenite, pyrite, arsenopyrite, chalcopyrite, bornite) have been found to provide reliable Re-Os ages, whereas some do not (pyrrhotite, sphalerite).

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Luminescence Dating, Single-Grain Dose Distribution

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Synonyms

Single-grain D_e distribution; Single-grain equivalent dose distribution

Definition

A single-grain dose distribution refers to the spread in measured dose values (and their associated uncertainties) for individual mineral grains in luminescence dating; usually these are independent dose estimates for tens to hundreds of single grains from the same sample.

Introduction

In luminescence dating, an estimate is made of the equivalent dose for a single grain or for a group of mineral grains, the latter commonly referred to as an “aliquot.” The equivalent dose (expressed in grays, Gy) corresponds to the radiation energy absorbed by a mineral grain, and stored in the form of trapped electrons, since the grain was last exposed to sunlight (“bleached”) or was last heated to a high temperature. But this only holds true for an aliquot if each and every grain on the aliquot had been bleached or heated to the same, sufficient extent. For this reason, a single grain is the smallest meaningful unit of analysis in luminescence dating, because each grain in a sample may, in principle, have had a different bleaching, heating, or postdepositional history.

An equivalent dose estimate for a single grain, or for a single aliquot composed of multiple grains, is obtained experimentally, so it has an associated uncertainty. The uncertainty is usually expressed as the standard error, at the 1-sigma (1σ) or 68 % confidence interval. The estimate of uncertainty is as important as the estimate of the equivalent dose itself, and this is especially true for single grains, because the size of the uncertainty can vary greatly from grain to grain. A set of bivariate observations (of equivalent dose and standard error) are, therefore, commonly obtained for each sample, and the distribution of these observed values should be examined before calculating the burial age of the sample or some other event of interest.

As a general note of caution, it is important to ensure that the quoted standard error encapsulates all of the measurement uncertainties associated with estimation of the equivalent dose. For single grains, the standard error includes uncertainties associated with photon counting statistics, instrumental reproducibility, mathematical fitting of the dose–response curve to the measured luminescence data, and corrections for any spatial heterogeneity in the laboratory beta sources. Equivalent dose values might appear more scattered than is actually the case if the standard errors are

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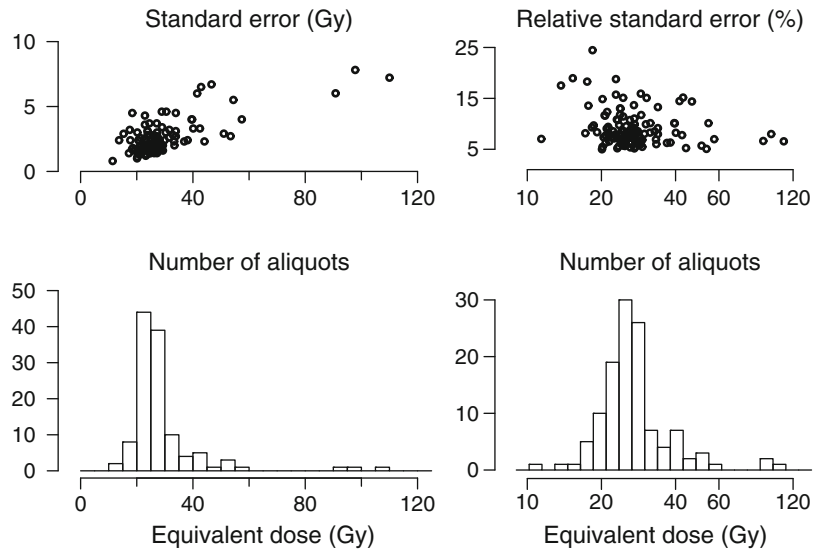


Fig. 1 Histograms of equivalent dose values and scatter plots of their standard errors for 120 single aliquots of a fluvial sample. The plots in the *left-hand* column use a linear scale for the equivalent dose and show the absolute standard errors in Gy. The *right-hand* panels use a logarithmic scale for the equivalent dose (i.e., equal divisions of log dose) and show the relative standard errors in % (From Galbraith and Roberts (2012))

underestimated, whereas dose distributions may look misleadingly homogeneous if the standard errors are overestimated.

Graphical Displays of Equivalent Dose Distributions

Researchers often wish to plot the distribution of equivalent dose estimates, and there are several means of doing so. Galbraith and Roberts (2012) review some of the most popular approaches to displaying equivalent dose values.

Frequency Distributions

A commonly used form of data display is the histogram. This requires equivalent dose values to be sorted into “bins” of some fixed size and then the number of observations summed for each bin to generate a frequency distribution. In Fig. 1, the bottom left-hand plot is a histogram of the equivalent dose values for 120 aliquots composed of sand-sized quartz grains from a fluvial sample. Most values cluster between 20 and 30 Gy, with a few smaller values and some much larger ones. The distribution appears to be asymmetric and positively skewed.

Despite their apparent simplicity, however, histograms present various problems of implementation and interpretation. The bin size, for example, is an arbitrary choice, so the shape of the histogram can be affected by the choice of bin size. Furthermore, equivalent dose histograms include information about the distribution of the “true” doses (i.e., the doses that would have been observed if we could do so without measurement error) and the distribution of the standard errors, among other things.

In Fig. 1, the chosen bin size is 5 Gy. This is larger than the standard errors for most of the equivalent dose estimates, which are displayed in the top left-hand plot. The combination of these two plots is useful, as it allows the reader to see the distribution of equivalent doses and the size of their standard errors, which is not something that can be judged from the histogram alone. The

standard errors of this sample show an interesting feature that is typical of many luminescence samples: the size of the uncertainty increases with the size of the equivalent dose. Because of this, larger equivalent dose values will tend to scatter more in a histogram than smaller values and thereby create a positive skew, regardless of the bleaching and burial history of the grains.

To compensate for this effect, it is useful to take the natural logarithm of each equivalent dose value and to express the standard error as the relative standard error (i.e., the standard error in Gy divided by the equivalent dose in Gy). Logarithmic transformations are commonplace in statistics and exploit the fact that the relative standard error of an estimate is approximately equal to the absolute standard error of its natural logarithm.

The two right-hand plots in Fig. 1 show the same data as in the left-hand column but with the relative standard errors plotted in the top right-hand panel and the equivalent doses presented on a logarithmic scale. The relative standard errors do not increase with the size of the equivalent dose, and the equivalent dose distribution is much closer to normal (Gaussian) in shape. As the latter may be interpreted differently from the bottom left-hand histogram, it is worthwhile displaying data in different ways before drawing conclusions about the likely bleaching and burial history of a sample from its equivalent dose distribution.

Another form of the histogram, often referred to as a “probability density function,” is sometimes used in luminescence dating. Probability density functions have the appealing appearance of “smoothed” histograms, but they suffer from many statistical shortcomings, and their use is strongly discouraged (Galbraith 1998, 2010; Galbraith and Roberts 2012).

Radial Plots

The preferred form of data display for equivalent dose values is the “radial plot” (Galbraith 1988; Galbraith et al. 1999; Galbraith and Roberts 2012). This plot is particularly useful to display single-grain (and single-aliquot) dose distributions because both the equivalent dose value and its standard error are shown for each and every grain (or aliquot), and this allows a number of other features of the distribution to be discerned at the same time. Figure 2 is a radial plot of the same data as shown in Fig. 1. Each of the open circles denotes the equivalent dose value and relative standard error for a single aliquot. The equivalent dose can be read by drawing a line from the zero point on the “standardized estimate” axis (on the left-hand side), through the data point of interest, to intersect the radial axis on the right-hand side. The point of intersection is the equivalent dose (D_e). The relative standard error on this estimate is read by drawing a vertical line from the same data point to intersect the horizontal axis at the bottom. The relative standard error is shown in % (i.e., as the standard error divided by the equivalent dose, multiplied by 100), and the “precision” is the reciprocal of the relative standard error.

A benefit of displaying the data in this form is that the equivalent dose values measured with the highest precision (i.e., the smallest relative standard errors) fall furthest to the right, whereas those measured with least precision lie furthest to the left. In addition to this self-sorting of values by precision, the use of the standardized estimate allows other aspects of the distribution to be conveniently assessed at a glance. The standardized estimate represents the unit standard deviation applicable to all of the data points. For each point, it is calculated as the equivalent dose minus a chosen reference value (such as the average equivalent dose for the entire distribution), divided by the relative standard error for that point. Accordingly, any band of width ± 2 units projecting from the standardized estimate axis will capture 95 % of the points if they are statistically consistent at 2σ .

In Fig. 2, the equivalent doses are plotted on a log scale (as in the right-hand panels of Fig. 1), so the standardized estimates and relative standard errors are based on the log equivalent dose values. Clearly, no single band extending ± 2 units from the standardized estimate axis can capture 95 % of

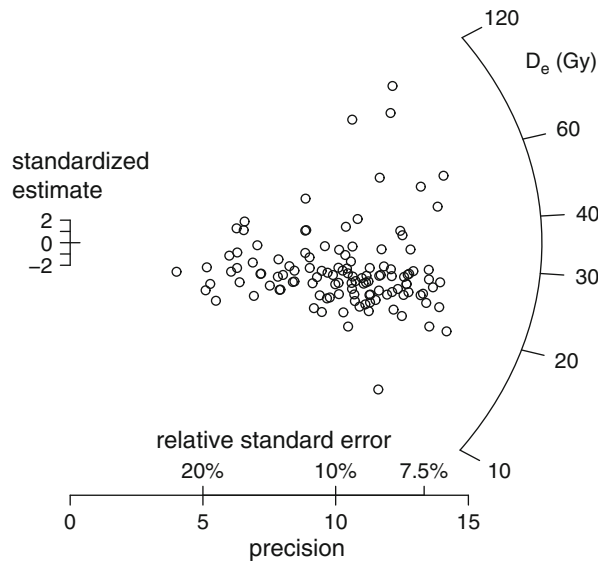


Fig. 2 A radial plot of the same data as displayed in Fig. 1. The equivalent dose values are plotted on a log scale, and the relative standard errors (in %) are indicated on the horizontal axis (From Galbraith and Roberts (2012))

the equivalent dose values, so there is some additional spread, which can be expressed in terms of the “overdispersion.” The latter term is used to describe the scatter among the equivalent dose values over and above that due to the measurement error associated with each observation (Galbraith et al. 2005; Galbraith and Roberts 2012). The data in Fig. 2 are overdispersed by $32.0 \pm 2.3\%$, as calculated from the “central age model” (see below). Two other noteworthy features of this distribution are visually apparent. First, there is a high density of data points consistent with equivalent dose values of 20–30 Gy, so the “frequency” aspect of the histogram is inherent in the radial plot also. Second, the plot shows clearly the existence of three very high equivalent dose values and one very low value, each measured with reasonable precision (i.e., a relative standard error of less than 10 %).

The use of log values may not be appropriate for young samples that contain grains with equivalent dose values close to zero or negative dose estimates within error of zero. In such instances, the unlogged or modified log-transformed versions of the radial plot can be used (Arnold et al. 2009; Galbraith 2010; Galbraith and Roberts 2012). Example radial plots for samples deposited in a variety of contexts are provided by Jacobs and Roberts (2007) and Galbraith and Roberts (2012), the latter summarizing the many appealing features of radial plots as follows:

- Equivalent dose values can be viewed simultaneously with their standard errors.
- Data are sorted automatically so that the equivalent dose values can be distinguished easily in terms of their relative precisions.
- Any overdispersion can be identified at a glance.
- Patterns in the data, such as the clustering of equivalent dose values, the presence of outliers, or the existence of multiple, discrete dose components (see below), can be recognized before calculating the sample age.

Age Models for Equivalent Dose Distributions

After a visual inspection of the equivalent dose distribution, it is common for researchers to then estimate the equivalent dose for the population of grains (or aliquots) related most closely to the

event of interest. This may be the burial time of the most fully bleached grains in the sample or the last time that the grains were heated to a high temperature. In sediment dating, the value often sought is the equivalent dose corresponding to the most recent bleaching event. But if a sample had been disturbed after burial and become contaminated by younger or older intrusive grains, then it is useful to be able to identify and exclude these grains before calculating the sample age.

To allow for these and other possibilities requires a range of models based on sound statistical principles. Several parametric models, developed originally for fission track dating (Galbraith and Green 1990; Galbraith and Laslett 1993), have been adapted for luminescence data and are now in widespread use. Galbraith and Roberts (2012) review these different “age models,” although it should be borne in mind that they are rarely applied to ages per se in luminescence dating. Instead, these models are applied to equivalent dose values, because the information required to determine single-grain ages – namely, the environmental dose rate specific to each grain – is not generally known. At present, the same (sample mean) dose rate is usually employed for all grains, while research continues into methods of measuring and modeling grain-specific dose rates.

A critical element of any decision-making process involving statistical models is sample context. This should dictate which, if any, of the models may be the most appropriate for the sample of interest. On the basis of its depositional context, for example, one could ask if a sample is likely to have been fully or incompletely bleached at the time of deposition. Similarly, one could consider if there is any independent evidence that the stratigraphic integrity of the site has been compromised, perhaps resulting in postdepositional disturbance of the sample. In short, statistical models should not be applied without first taking into account the archaeological or geologic context of a sample, stratigraphic considerations, and other relevant information, such as independent age control (Galbraith et al. 2005; Galbraith and Roberts 2012).

Common and Central Age Models

These two models represent the most straightforward case in luminescence dating: one in which the “average” equivalent dose is the quantity of interest. This may be a useful value to estimate for samples composed of grains that have been well bleached before deposition, exposed to the same environmental dose rate after burial, and remained unaffected by any processes of postdepositional sediment mixing. The equations for the common and central age models are given in Galbraith et al. (1999) and Galbraith and Roberts (2012), together with worked examples in the former. The two models are identical insofar as they both weight each equivalent dose by the inverse square of its standard error, which is a standard statistical method of averaging values with differing precisions. A major difference, however, is that the central age model also calculates – and explicitly includes in the standard error – the extent of any overdispersion among the equivalent dose values. If there is zero overdispersion (i.e., all of the spread among the equivalent doses can be accounted for by the individual measurement uncertainties alone), then the central age model reduces to the common age model. But even for samples of quartz grains that are known or are thought to have been fully bleached at deposition, overdispersion values of 10–20 % are commonplace (Galbraith et al. 2005; Jacobs and Roberts 2007; Arnold and Roberts 2009), so the central age model is usually the more appropriate of the pair.

As illustrated by comparing the two lower plots in Fig. 1, log equivalent doses typically produce a much closer approximation to a normal (Gaussian) distribution than do their unlogged counterparts. This is due to the size of the absolute standard error increasing in concert with the equivalent dose (see top left-hand panel), a common feature of many luminescence samples. For this reason, the most widely used form of the central age model utilizes log equivalent dose values and the relative standard errors; the resulting model estimate of equivalent dose approximates the geometric mean. If

the measured equivalent doses are zero or negative, as can occur with some young samples and with modern samples, then log transformations are not applicable, and the unlogged version of the central age model could be used instead (Arnold et al. 2009).

Minimum Age Models

The assumption of complete bleaching before deposition and lack of disturbance thereafter will not be true for many samples. For example, sediment grains transported underwater may not be fully bleached, and some deposits may be subject to bioturbation or human disturbance. In such cases, the “average” equivalent dose will be of little interest. For samples that are thought to contain some grains that were fully bleached before deposition and others that were only partially bleached, the minimum age model can provide a useful means of estimating the equivalent dose associated with the subset of well-bleached grains. Details of this model are given in Galbraith et al. (1999) and Galbraith and Roberts (2012). Alternative approaches that are philosophically similar to the minimum age model are rarely based on well-established statistical principles, so the statistical properties of the resulting equivalent dose and uncertainty estimates are ambiguous, at best.

The most widely used version of the minimum age model assumes that the log equivalent doses form a truncated normal distribution, with the lower truncation point corresponding to the average log dose of the subset of fully bleached grains. This assumed distribution is one of several that could be made, but it is convenient to assume a normal distribution in the absence of independent support for another type. The minimum age model was originally developed with four adjustable parameters, but it has been shown that data sets with small numbers of equivalent dose values or less dispersed distributions are often fitted better using a three-parameter model, in which the lower truncation point equals the mean of a normal distribution. As with the central age model, the unlogged version of the minimum age model may be more appropriate for samples with zero or negative measured equivalent doses (Arnold et al. 2009).

When implementing the minimum age model, allowance needs to be made for the extent of inherent overdispersion among the equivalent dose values of the subset of fully bleached grains. That is, well-bleached samples commonly exhibit some amount of overdispersion in their equivalent dose values, so an estimate of this overdispersion should be added to the relative standard error of each equivalent dose before running the model. This estimate could be obtained from a well-bleached sample of the same mineral that is similar in age and derived from the same source. In the absence of independent data, one could conduct a sensitivity test of the model using overdispersion values of 10 % and 20 %, for example.

Minimum age models have been tested in numerical simulations and in comparisons against independently dated Holocene samples from a variety of geomorphic settings (Olley et al. 2004; Arnold et al. 2009). The latter studies utilized single grains of quartz, but the minimum age model can also be applied to single aliquots with one additional caveat: the estimate of the minimum dose may still be larger than the equivalent dose of the most recently bleached grains unless at least one aliquot consists entirely of fully bleached grains. For aliquots composed of relatively few fully bleached grains, the minimum dose may be much too large, and single-grain analysis may be required to obtain an accurate estimate of depositional age.

Finite Mixture Model

For some samples, neither the mean nor minimum estimates of equivalent dose may correspond to the event of interest. This may be so for deposits affected by bioturbation or for sites disturbed by human activities, both of which may result in mixing of grains between units of different ages. In such circumstances, the finite mixture model may be able to discern the existence of multiple,

discrete components in a single-grain equivalent dose distribution (Roberts et al. [2000](#); Galbraith and Roberts [2012](#)).

In the finite mixture model, the log equivalent doses for single grains are assumed to represent a mixture of discrete populations, each of which is normally distributed with the same relative overdispersion. The extent of overdispersion is one of the parameters in the model, as is the number of discrete populations. In practice, the model is run by initially fixing the number of components at 2 and then inserting some reasonable overdispersion values (such as 10 %, 15 %, and 20 %). The number of fitted components is then increased to 3, using the same overdispersion values as previously, and so on. The model uses maximum likelihood to estimate the mean equivalent dose and standard error for each fitted component and the proportion of grains in each component. When the number of components is set at 1, the finite mixture model is mathematically identical to the central age model.

The goodness-of-fit of the model to the data can be assessed using the Bayes Information Criterion (BIC), which takes into account the maximum likelihood estimates and the number of fitted components; the smallest BIC indicates the minimum number of components needed to explain the dose distribution. It is important to also check that the model estimates are sensible and to compare them with the distribution of equivalent doses on a radial plot, as no model should be used as a “black box.” Straightforward explanations and worked examples of the finite mixture model fitting procedure are given in David et al. ([2007](#)) and Jacobs et al. ([2008](#)).

For 2- and 3-component mixtures of single grains that were bleached and then given known laboratory doses, the model could successfully recover the correct number of discrete components, their relative proportions, and the corresponding equivalent dose values, provided the overdispersion parameter was small, known, or similar for each component (Roberts et al. [2000](#); Jacobs et al. [2006](#)). But the finite mixture model may be unable to identify discrete components in more complex equivalent dose distributions, such as those associated with heterogeneously bleached grains that have been mingled subsequently. The model should also not be applied to the equivalent dose distributions of multigrain aliquots, even for those consisting of very few grains. If aliquots contain luminescent grains from more than one parent population, then “phantom” components with intermediate doses can easily be generated – that is, equivalent dose components that are not present in any of the single-grain parent populations (Arnold and Roberts [2009](#)).

Summary or Conclusions

The graphical display of single-grain or single-aliquot equivalent dose values can be accomplished in various ways, of which the radial plot provides an effective means of assessing all of the salient information at a glance. After an initial visual inspection of the distribution, one or more statistical “age models” can be used to estimate the equivalent dose for the population of grains (or aliquots) related most closely to the event of interest. Such models should be supported by well-established statistical theory, but the choice of model depends fundamentally on the scientific context of each sample and on the purpose of the investigation (Galbraith and Roberts [2012](#)).

Cross-References

- [Luminescence Dating](#)
- [Luminescence Dating, Uncertainties, and Age Range](#)

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Molecular Rate Variation (Molecular Clocks)

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Molecular Rate Variation

The rate of molecular evolution is the rate at which substitutions accumulate in an organism's genome. Rates of molecular evolution can vary dramatically, for example, the rate of molecular evolution in some viruses is around one substitution per base pair per 1,000 years (Pagán et al. 2010), while in mammals the rate is around one substitution per base pair per 1,000 million years (Nabholz et al. 2008). Even closely related plants and animals can have rates of molecular evolution that vary by more than an order of magnitude (Thomas et al. 2006; Smith and Donoghue 2008; Welch et al. 2008; Lanfear et al. 2013). Accounting for molecular rate variation is important in methods that use molecular sequence data to date the divergences between species (molecular dating).

There has been a great deal of research into the causes of variation in rates of molecular evolution. This research has identified a range of factors which may cause variation in the rate of molecular evolution (Bromham 2011), and these factors can be broken up into those that affect the mutation rate and those that affect the rate at which new mutations are fixed in a population (the fixation rate). An increase in either the mutation rate or the fixation rate can potentially increase the overall rate of molecular evolution, although there are some situations in which these increases will leave the rate of molecular evolution unchanged (de Visser et al. 1999).

Many factors have been suggested to increase mutation rates in DNA sequences, including temperature, UV radiation, oxygen radicals, recombination, genome copying, and natural selection (Martin and Palumbi 1993; Davies et al. 2004; Wright et al. 2006; Lanfear et al. 2007; Thomas et al. 2010; Hodgkinson and Eyre-Walker 2011; Wright et al. 2011; Lourenço et al. 2013; Lanfear et al. 2013). In principle, variation in any of these factors could cause variation in the rates of molecular evolution between species, although the evidence for this is weak for UV radiation and oxygen radicals in particular (Davies et al. 2004; Lanfear et al. 2007; Joyner-Matos et al. 2011; Lanfear et al. 2013). However, there is good evidence that the many mutations occur during genome-copying events (meiosis and mitosis) and that variation in long-term rates of genome copying may explain much of the variation in the rates of molecular evolution between species (Smith and Donoghue 2008; Welch et al. 2008; Thomas et al. 2010; Lanfear et al. 2013). Intriguingly, it has also been suggested that natural selection may play a role in determining mutation rates and rates of molecular evolution, either through selection for increased longevity (Nabholz et al. 2008; Welch et al. 2008; Galtier et al. 2009) or through the reduced efficacy of natural selection in small populations (Lynch 2010, 2011).

Anything that increases the fixation rate of new mutations can also increase the substitution rate. Two factors combine to determine the fixation rate of a new mutation: the effect of that mutation on the carrier's fitness and the effective population size of the host population. As fitness effects

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become more beneficial and effective population sizes get larger, fixation rates increase (Woolfit 2009). This is because a population's effective population size determines the balance of power between natural selection and genetic drift. The larger the effective population size, the stronger natural selection is relative to genetic drift, and the faster beneficial mutations are fixed in the population, and deleterious mutations removed. Because we expect most mutations to be deleterious, it is generally thought that organisms with smaller effective population size should have faster rates of molecular evolution. Some studies have supported this idea and have shown that organisms with smaller effective population sizes tend to evolve more quickly, at least by some measure of the rate of molecular evolution (Moran 1996; Woolfit and Bromham 2003, 2005). However, other results suggest that the relationship between population size and the rate of molecular evolution can be much more complex than this simple model suggests (Charlesworth and Eyre-Walker 2007; Wright et al. 2009).

We have a fairly good understanding of the most important causes of variation in rates of molecular evolution. But despite this, we can often explain less than half of the variation that we can measure, suggesting that we still have a lot to learn. A better understanding of molecular rate variation is important because it can help improve molecular dating methods. Perhaps the best example of this is the development of new methods which leverage what we know about the causes and correlates of molecular rates to directly improve our estimates of divergence dates from DNA sequence data (Lartillot and Poujol 2011; Lartillot and Delsuc 2012). As our understanding of molecular rate variation continues to increase, we will be able to continue to improve the accuracy of molecular dating methods.

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Acasta Gneiss Complex

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Synonyms

[Acasta gneisses](#)

Definition

The Acasta gneiss complex in northwestern Canada contains some of the oldest dated rocks on earth and the oldest dated using U-Pb in zircon. They therefore potentially preserve clues to the nature and history of earth's oldest crust. The geology of the gneisses reflects a complex multistage history of magmatism, metamorphism, and deformation over more than 400 million years, and the entire complex should be viewed as a small fragment of Hadean to Archean continental crust. The gneisses are compositionally diverse and range from granite and tonalite to gabbro and serpentinized ultramafic rocks. The oldest published crystallization age. There are isotopic and inherited zircon data consistent with the involvement of crust as old as 4.2 Ga. There is no single age of the Acasta gneiss complex (Bowring and Williams 1999).

Introduction

Components of the Acasta gneiss complex are among the oldest known rocks on earth. They are exposed in northwestern Canada (65° 10' N and 115° 30' W) along the western margin of the Archean Slave craton (>2.58 Ga), in the core of a north-trending fold in the foreland of the Wopmay orogen, a 2.02–1.84 Ga-old orogenic belt. The Acasta gneisses range in age from 4.03 to ca 3.6 Ga (Bowring and Williams 1999; Iizuka et al. 2006, 2007; Stern and Bleeker 1998). All age groups are compositionally diverse and range from granite to quartz diorite to tonalite. The deformational history is complex with several episodes resulting in well-developed foliations. In low-strain domains, crosscutting relationships can be observed (Fig. 1), but in general, deformation has obscured primary relationships between different rock types. Lens-shaped boudins of serpentinized ultramafic rocks occur throughout the gneisses; some are 100's of meters in long dimension. No ca. 4.0–3.6 Ga metasedimentary rocks have been discovered although sparse outcrops of quartzite, iron formation, and pelite are found locally tightly folded into older gneisses. A wide variety of weakly deformed granitic dikes that intrude older gneisses are ca 3.6, 3.4, 2.9, and 2.6 Ga (Stern and Bleeker 1998; Bleeker and Stern 1997). During 1.88 Ga Calderian orogeny to the west, thrust sheets of 1.9–2.5 Ga rocks were thrust over the western edge of Slave craton resulting in a set of north-trending folds and metamorphism of underlying Archean rocks. Ar-Ar biotite and U-Pb

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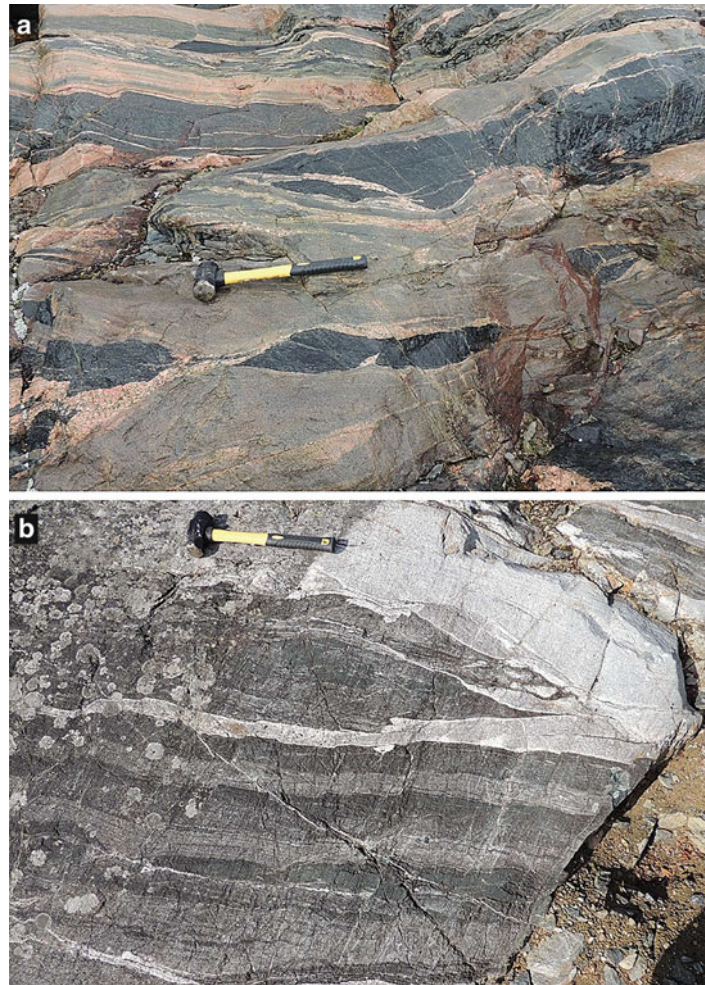


Fig. 1 Outcrop photos of ancient gneissic rocks of the Acasta gneiss complex, Acasta River area, N.W.T. **(a)** Layered multicomponent gneiss consisting of tonalite (*dark grey*), granodiorite (*grey*), and granite (*pink*) layers. **(b)** Layered tonalite-granodiorite gneiss crosscut by multiple generations of younger granite

apatite dates record complex reheating and cooling during this event and are as young as ca 1.77 Ga (Sano et al. 1999)

Age Constraints

U-Pb geochronological studies indicate that the Acasta gneisses range in age from 4.03 to ca. 3.6 Ga with distinct groupings at 4.03–3.94, 3.74–3.72, and 3.66–3.58 Ga, although this may be an artifact due to a relatively small number of published analyses. U-Pb zircon dates indicate that the oldest igneous crystallization ages for Acasta gneiss protoliths that range from granite to tonalite/diorite are 4.012 ± 0.006 to 4.030 ± 0.003 Ga. Many zircons from all rock types contain older cores with the oldest at 4.065 ± 0.016 and 4.2 Ga (Iizuka et al. 2006), consistent with the involvement of even older crust in their generation by partial melting or assimilation (Bowring and Williams 1999). In general, the geochemistry of the Acasta gneisses is not distinctive from other Archean and younger rocks; they are on average enriched in light rare-earth elements with variable depletion in heavy rare-earth elements thought to reflect the involvement of garnet in the source area. Radiogenic isotope

systematics in whole rocks (Sm-Nd) and zircon (Lu-Hf) are also consistent with the involvement of older continental crust. Many of the rocks have zircons with thin overgrowths likely related to episodes of metamorphism that range from 3.8 to 3.4 Ga.

Concluding Remarks

The formation and preservation of continental crust early in earth history is of broad interest to earth and planetary scientists as the oldest continental crust records the only history of magma formation and the role of water in generating granitic magmas more than 4 billion years ago. With estimates for the age of the earth-moon system between 4.5 and 4.4 Ga and the oldest detrital zircon from Australia, 4.374 ± 0.0006 Ga (Valley et al. 2014), the Acasta gneiss complex with igneous rocks as old as 4.030 Ga with evidence for involvement of even older crust offers important insights into early crustal evolution. Finally, many of the rocks in the Acasta gneiss complex are very similar in composition to those formed much later in earth history by plate tectonic processes, and there is no compelling evidence of the late heavy bombardment (Mojzsis et al. 2014) preserved in the Acasta gneisses.

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Molecular Clocks

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Definition

Molecular clock. A hypothesis that predicts a constant rate of molecular evolution among species. It is also a method of genetic analysis that can be used to estimate evolutionary rates and timescales using data from DNA or proteins.

Introduction

The tempo and mode of evolution are central themes of biological research. This places importance on the estimation of evolutionary timescales, which provide the backdrop for our interpretations of evolutionary patterns and processes. Traditionally, such inferences were made from the fossil record, coupled with radiometric dating. Fossils can provide an estimate of when different lineages first appeared and when species diverged from each other. In many cases, however, such data are unavailable, forcing us to look elsewhere for a source of temporal information. The “molecular clock,” proposed in the 1960s (Zuckerkandl and Pauling 1962, 1965), allows evolutionary time-scales to be estimated using genetic data. Molecular clocks have provided insights into significant evolutionary events such as human evolution and the radiations of birds, mammals, and flowering plants. Molecular-clock methods continue to undergo improvement, which is crucial if we are to take advantage of the growing wealth of genomic data (Kumar 2005).

The molecular-clock hypothesis posits that rates of molecular evolution, as reflected in changes in DNA or protein sequences through time, are constant among lineages (but not across different regions of the genome). Nucleotide mutations cause DNA sequences to change over time, whereas mutations of amino acids lead to evolution in proteins. These mutations occur with a constant probability rather than at a constant frequency – that is, the molecular clock is stochastic rather than metronomic (Zuckerkandl and Pauling 1965). The occurrence of mutations in a DNA sequence is often modelled using a Poisson process.

A corollary of the molecular-clock hypothesis is that the genetic difference between any two species is proportional to the time since they last shared a common ancestor. This is a useful relationship because it allows evolutionary timescales to be estimated from genetic data, provided that the rate of molecular evolution is known. The molecular clock represents the only method for studying the evolutionary timescales of organisms that have failed to leave any trace in the fossil record, including many groups of invertebrates, bacteria, and viruses. It also allows us to estimate the timing of events that are too recent to be resolved by fossil evidence, such as divergences among conspecific populations (Arbogast et al. 2002).

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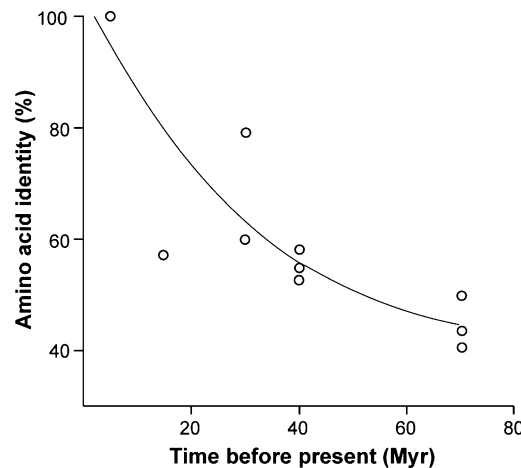


Fig. 1 Plot of amino acid identity of fibrinopeptides from various pairs of mammals, plotted against time since divergence. The divergence times are based on estimates from the fossil record (Data are from Doolittle and Blomback (1964))

History of the Molecular Clock

The molecular-clock hypothesis was put forward by Emile Zuckerkandl and Linus Pauling (1962), who assumed a constant evolutionary rate in their analysis of globin proteins from vertebrates. They observed about 18 differences in amino acids between horse and human and estimated the mutation rate by assuming that the divergence between these two species occurred 100–160 Ma ago. Upon extrapolating this rate, Zuckerkandl and Pauling (1962) estimated that humans diverged from gorillas about 11 Ma ago. They also estimated that different copies of globin genes first diverged from each other in the late Precambrian. When reporting these estimates, Zuckerkandl and Pauling (1962) warned about the possible confounding effects of a number of factors, including natural selection, variations in population size, and mutational saturation.

In the following years, further studies produced evidence of clocklike evolution in other proteins. Doolittle and Blomback (1964) found a simple relationship between sequence identity and time since divergence in mammalian fibrinopeptides (Fig. 1). A year later, Zuckerkandl and Pauling (1965) coined the term “molecular evolutionary clock.” It promised to be a useful tool in biological research, as demonstrated shortly afterward by Sarich and Wilson (1967a, b) in their pioneering studies of the evolutionary timescale of hominids and other primates.

At the time, the idea of a constant substitution rate was controversial (Morgan 1998). The molecular clock was received unenthusiastically by George Gaylord Simpson (1964), among others. Criticisms of the molecular clock were partly motivated by the apparent lack of uniformity in the pace of morphological evolution, which was presumably linked to molecular evolution. There was no evidence to suggest that adaptive change occurred at a uniform rate and it seemed implausible that the complex process of molecular evolution could be described by such a simple statistical model.

Meanwhile, there was growing evidence of high evolutionary rates in various proteins, suggesting that a large proportion of the changes in amino acids must have a negligible impact on evolutionary fitness. As a response, Motoo Kimura (1968) proposed the neutral theory of molecular evolution, which states that many mutations have such a small effect on the fitness of an organism that they can be considered as “neutral.” This can be explained by the fact that many amino acids in a protein can be exchanged for other amino acids with similar biochemical

properties, with negligible impact on the overall function or structure of the protein. At the level of DNA, many mutations in protein-coding genes are “synonymous” because they do not result in any changes in the amino acid sequence of the protein. The fate of these “neutral” mutations is determined stochastically by a process known as genetic drift. The neutral theory was proposed independently by Jack King and Thomas Jukes (1969), who cited a range of evidence to support their hypothesis.

One of the predictions of the neutral theory is that rates of molecular evolution are constant among lineages. However, this prediction refers specifically to the rate of genetic change per generation. As a consequence, we expect to see a generation-time effect, whereby species with shorter generations tend to evolve more quickly per unit of time. For example, a higher rate would be observed in rodents than in whales. This is based on the assumption that most mutations occur during the replication of germline DNA. Such a generation-time effect was observed in the analyses of non-coding DNA (Laird et al. 1969; Kohne 1970). This was in contrast with the rate of protein evolution, which appeared to be independent of generation time.

In response to the shortcomings of the neutral theory, Tomoko Ohta (1972, 1973) proposed the nearly neutral theory of molecular evolution. In this framework, there is a large class of “nearly neutral” mutations that have small effects on an organism’s fitness. In contrast with the results of the neutral theory, the nearly neutral theory states that the population sizes of species have a significant influence on the molecular evolutionary process. Many mutations are slightly harmful and are gradually removed from the population. In large populations, natural selection is effective at removing mutations that are detrimental to the organism’s fitness. In small populations, natural selection tends to be ineffective and most genetic change is driven by genetic drift. Generally, drift acts more quickly in small populations than does selection in large populations. However, a greater number of mutations appear each generation in large populations, simply because there are more individuals that can experience mutations. These two effects offset each other, leading to a relatively constant evolutionary rate among species per unit of time.

Through the ensuing decades, the molecular clock was used to study the evolutionary timescales of a range of organisms. Some of the most prominent studies involved analyses of the metazoan evolutionary timescale, with a focus on the divergences among animal phyla. In considerable conflict with the “Cambrian explosion” scenario supported by the fossil record, estimates from the molecular clock suggested a protracted Precambrian timescale for basal metazoan divergences (e.g., Dickerson 1971; Runnegar 1982; Doolittle et al. 1996). Similarly, molecular evidence pointed to much deeper diversifications of avian and mammalian orders than those suggested by paleontological evidence (e.g., Cooper and Penny 1997; Springer 1997). These discrepancies remain some of the key sources of debate about the accuracy of the molecular clock (Bromham and Penny 2003).

Meanwhile, there was a growing body of evidence that pointed to rate variation among lineages. This came partly from various statistical tests that had been developed to test for clocklike evolution in genetic data (Wu and Li 1985; Tajima 1993). Departures from the molecular clock provided a challenge for studies of evolutionary timescales. It was not until the late 1990s, however, when molecular-clock methods were developed that were able to account for variation in evolutionary rates (Sanderson 1997; Thorne et al. 1998). Known as “relaxed” molecular clocks because they relax the assumption of rate constancy among lineages, these have become the standard techniques in molecular evolutionary analysis.

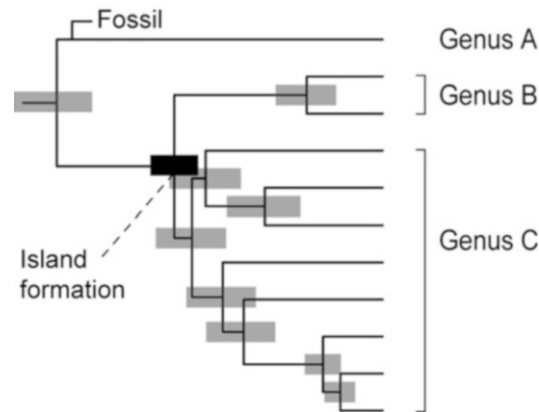


Fig. 2 Phylogenetic tree showing the relationships of species from three genera, A, B, and C. Genera A and B are found on the mainland, whereas species of *Genus C* are found on an offshore island that was formed by volcanic activity. The tree is drawn to an unspecified timescale, so that the branch lengths are proportional to time. The tree illustrates the use of two molecular-clock calibrations. First, a fossil taxon has been assigned to the lineage leading to *Genus A*. This places a minimum age constraint on the divergence of A from B and C. Second, a geological calibration is placed on the divergence between B and C. The split between these genera is assumed to coincide with the formation of the offshore island on which *Genus C* is found. The age of the island is estimated using radiometric dating. The uncertainty in this date estimate is incorporated into the calibration, as indicated by the *black bar*. *Gray error bars* represent the uncertainty in the molecular-clock estimates of lineage divergence times

Rates of Molecular Evolution

Absolute rates of molecular evolution vary among regions of the genome because of differing constraints. Functionally important genes often evolve at an extremely slow pace, because many new mutations are detrimental to the organism and are rapidly removed by natural selection. As a consequence, such genes are often conserved even among distantly related organisms, making them useful genetic markers for studying deep evolutionary relationships. For example, histones, which are proteins that play an important role in binding and packaging DNA, have a very low substitution rate. In contrast, non-coding DNA has fewer functional constraints and can evolve at a higher rate than protein-coding DNA.

The mitochondrial genome evolves rapidly in animals and experiences about 10^{-8} substitutions per nucleotide per year, which is an order of magnitude higher than the average rate in the nuclear genome. This is in contrast with the pattern of molecular evolution in plants, where nuclear genomes evolve more quickly than either chloroplast or mitochondrial genomes. Rates of change in the genomes of viruses are higher by several orders of magnitude. In rapidly evolving RNA viruses, such as influenza virus and human immunodeficiency virus (HIV), mutation rates can exceed 10^{-3} mutations per nucleotide per year, and measurable genetic change can occur over a matter of weeks.

There is substantial variation in rates of molecular evolution across the tree of life. This variation is possibly driven by biological factors such as generation time, population size, longevity, and body temperature, as well as abiotic factors such as ultraviolet radiation. The relative importance of each of these factors is still poorly understood (Bromham 2009). Studies have found evidence that molecular evolutionary rates are associated with longevity in mammals (Welch et al. 2008), with generation time in invertebrates (Thomas et al. 2010), and with height in plants (Lanfear et al. 2013). Research into the factors governing rate variation among organisms is ongoing.

Molecular Clocks and Phylogenetic Analysis

Molecular clocks are typically used in phylogenetic analyses, which aim to reconstruct evolutionary trees that show the relationships among species of interest (Fig. 2). Internal nodes in the tree represent evolutionary divergence events. The timing of these events can be estimated using molecular clocks. A number of statistical methods are available for testing the molecular-clock hypothesis for a given set of DNA or protein sequences. When the molecular clock is rejected for a data set, one can use a statistical model to account for rate variation when estimating evolutionary timescales (Welch and Bromham 2005).

When estimating evolutionary timescales in a phylogenetic analysis, the molecular clock needs to be “calibrated.” This can be done by assigning an absolute age to one or more nodes in the phylogeny, which can then act as a reference point for estimating the ages of the remaining nodes. Calibrations are often based on the fossil record, which can provide date estimates for the divergence events in the phylogeny (Fig. 2). If a fossil taxon can be reliably assigned to one of the lineages in the tree, then the divergence of that lineage from its sister lineage must be older than the age of the fossil. Calibrations can also be based on geological events, including the separation of continents or the emergence of islands, if they are linked to evolutionary divergences. An example of this might involve two sister genera, one of which is endemic to the mainland and the other endemic to an offshore island that formed as a result of volcanic activity (Fig. 2). The timing of the divergence between the two genera can be estimated by the age of the island which, in turn, can be estimated using radiometric dating. In some cases, previous genetic estimates of dates are employed as calibrations. These are known as “secondary” calibrations and are generally used when other calibrating information is unavailable.

Once the phylogenetic tree is calibrated by fixing or constraining the ages of one or more nodes in the phylogeny, the ages of the remaining nodes can be estimated using a molecular-clock analysis of the genetic data. This process is referred to as “molecular dating” or “divergence-time estimation.” There is a large range of methods and models that have been developed for this purpose, implemented in various statistical frameworks. These methods are available in a range of computer programs, including most standard phylogenetic software.

Universal Molecular Clocks

There is abundant evidence of evolutionary rate variation among species, dispelling any hope of a universal molecular clock across the tree of life. However, some researchers entertain the idea of homogeneous rates of mitochondrial evolution within certain groups of organisms, such as birds, mammals, and arthropods. This is a convenient assumption because it allows evolutionary rates to be applied in molecular-clock analyses when fossil or geological calibrations are otherwise unavailable.

Many studies of birds assume that the mitochondrial genome evolves at about 1 % per million years, a value that was initially based on a study of five species of geese (Shields and Wilson 1987). Various analyses of avian mitochondrial DNA have supported this estimate, including an extensive study involving 74 calibrations and genetic data from 12 orders of birds (Weir and Schluter 2008). The avian mitochondrial clock has been used to investigate key questions in the evolution of birds, including the impact of Pleistocene glaciation on the diversification of passerines. Some have questioned the reliability of this clock, citing evidence of significant rate variation among lineages

and across timescales (García-Moreno 2004; Ho 2007). Despite this criticism, the avian mitochondrial clock is still widely used.

In a similar fashion, a universal mitochondrial clock of 1 % per million years is often assumed for mammals. This rate was initially based on a mitochondrial study of primates and rodents (Brown et al. 1979), but it soon found support from estimates derived from other organisms (Wilson et al. 1985). Comprehensive analyses of mammalian DNA have demonstrated that there is substantial variation in rates among species, partly driven by differences in longevity (Nabholz et al. 2008; Welch et al. 2008).

Studies of evolutionary timescales in arthropods have often employed a rate of 1.15 % per million years, which is based on an analysis of insects and crustaceans (Brower 1994). This arthropod mitochondrial clock is widely used, partly because of the relative paucity of reliable fossil calibrations for many invertebrate taxa. However, this clock was based on a very small number of data points, leading to its validity being questioned (Papadopoulou et al. 2010; Ho and Lo 2013). Moreover, there is strong evidence of mitochondrial and nuclear rate variation among invertebrate species (Thomas et al. 2010).

The employment of “standard” mitochondrial clocks, such as those described above, has often been criticized. This is because the mitochondrial genome is subject to differing degrees of natural selection among species, which can lead to heterogeneity in evolutionary rates. Similar reasoning applies to evolutionary rates in the nuclear genome. Given that rates can show substantial variation even among closely related species, the use of standard clocks has the potential to yield date estimates that are highly misleading.

Controversies

The molecular clock has had a long history of controversy, beginning with the criticisms of the assumption of rate constancy and continuing with the debate over the relative merits of the neutral theory compared with natural selection. Current debates include the use of calibrations in genetic dating analyses and the constancy of evolutionary rates across timescales (Pulquério and Nichols 2007).

The choice of calibrations has a substantial influence on the outcome of a molecular-clock analysis. Inadequate modelling of calibrations can lead to highly misleading estimates of evolutionary timescales. Accordingly, recent work has focused on accounting for the uncertainty in fossil and geological calibrations (Ho and Phillips 2009). There is also ongoing development of methods for modelling and quantifying the uncertainty in fossil calibrations (e.g., Marshall 2008; Wilkinson et al. 2011). Some aspects of calibration methodology are poorly understood, such as the impact of using different methods for modelling the uncertainty in calibrations. One of the key points of agreement is that best practice involves the use of multiple calibrations throughout the phylogenetic tree.

The use of secondary calibrations in molecular dating has been the target of strong criticism (Graur and Martin 2004). Although the use of secondary calibrations is sometimes unavoidable, good practice involves taking into account the uncertainty in previous molecular-clock estimates. Ignoring this uncertainty can lead to artificially precise estimates of evolutionary timescales. Instead, the uncertainty should be incorporated into the dating analysis so that it can be included in the resulting estimates. This can readily be done in a Bayesian framework, in which the user can choose prior distributions that reflect the degree of uncertainty in the parameters and node times.

There is growing evidence that estimates of rates depend on the timescale of observation. Low rates of evolution are seen across long evolutionary time frames, such as those analyzed in phylogenetic analyses of distant species. In contrast, high evolutionary rates have been estimated in studies of populations and pedigrees (Howell et al. 2003). The exact causes of this disparity remain unclear, although they are likely to include the effects of natural selection and inaccurate modelling of the molecular evolutionary process (Ho et al. 2011). If the time dependence of molecular rates is not taken into account, evolutionary timescales can be under- or overestimated by an order of magnitude.

Conclusions

The molecular clock has undergone considerable evolution during its long history. It is useful as a hypothesis in molecular evolution and as a tool for estimating evolutionary rates and timescales. New molecular-clock methods are being developed in order to take advantage of the large amounts of genomic data that are being generated. With further refinement and development, the molecular clock will continue to play an important role in understanding the evolution of life on Earth.

Cross-References

- ▶ [Gene Sequencing](#)
- ▶ [Human Evolution \(Molecular Clocks\)](#)
- ▶ [Molecular Clock Calibrations](#)
- ▶ [Molecular Clocks, Relaxed Variant](#)
- ▶ [Molecular Dating of Evolutionary Events](#)
- ▶ [Molecular Rate Variation \(Molecular Clocks\)](#)
- ▶ [Polymerase Chain Reaction DNA Amplification](#)

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Molecular Clocks, Relaxed Variant

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Definition

Relaxed molecular clock. A statistical model of molecular evolution that allows the evolutionary rate to vary among organisms. Relaxed molecular clocks can be used to estimate rates and timescales of evolution using data from DNA or proteins.

Introduction

Evolutionary timescales can be estimated from genetic data using molecular clocks. The molecular clock hypothesis, developed in the early 1960s (Zuckerkandl and Pauling 1962, 1965), predicts a constant rate of evolutionary change among organisms. A natural consequence of this is a linear accumulation of genetic change over time, meaning that the genetic difference between two species is proportional to the time since they diverged from their most recent common ancestor. In some cases, the age of this divergence event can be inferred from independent data (such as fossil evidence), making it possible to estimate the rate of molecular evolution. If this rate is assumed to be constant among lineages (i.e., a “strict” or “global” molecular clock), we can use genetic data to estimate the divergence times for other species. Such analyses are normally done in a phylogenetic framework, which takes into account the evolutionary relationships among the organisms being studied. Most genetic dating methods assume that a reliable estimate of these evolutionary relationships is available.

Evidence of departures from clocklike behavior became apparent soon after the molecular clock was proposed (e.g., Laird et al. 1969). It is now generally accepted that genetic data rarely conform to a strict-clock model. A variety of statistical tests have revealed significant rate heterogeneity among lineages, even among closely related species. From a biological perspective, it is unsurprising to see such variation in molecular rates. Different species vary in body size, longevity, body temperature, generation time, and other heritable traits. Some of these factors have been shown to affect rates of molecular evolution (Bromham 2009). Even within species, such variation can be seen among populations. For example, different human populations have experienced differing demographic histories and are subject to heterogeneous environmental stresses, such that mutation rates vary among human lineages (Henn et al. 2009).

For several decades, the strict clock provided the only statistical framework for estimating evolutionary rates and timescales using genetic data. One of the first approaches for dealing with rate variation among lineages was to remove any data that violated the assumption of rate constancy (Li and Tanimura 1987; Takezaki et al. 1995). However, it is preferable to avoid discarding potentially valuable data and to model rate variation explicitly, particularly if it is an

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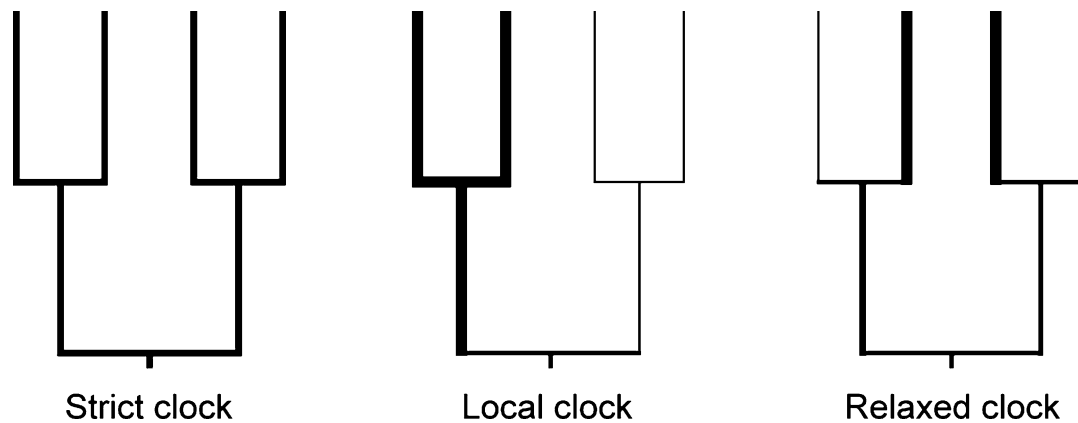


Fig. 1 Three different classes of molecular clocks are available. The thickness of each line reflects the magnitude of the evolutionary rate along a branch. *Strict or global clocks* assume a constant rate throughout the tree. *Local clocks* allow a limited number of rates throughout the tree. In this example, the left side of the tree has a different evolutionary rate from the right side of the tree. *Relaxed clocks* allow each branch in the tree to have a distinct evolutionary rate

integral property of the molecular evolutionary process (Gillespie and Langley 1979). Various methods have been developed to account for variation in molecular rates. They can be broadly divided into local molecular clocks and relaxed molecular clocks, which differ in how they assign rates to branches in the phylogeny (Fig. 1). Genetic dating methods that can accommodate such rate variation have been the subject of several reviews (Renner 2005; Welch and Bromham 2005; Rutschmann 2006).

Local Molecular Clocks

Local molecular clocks assume that evolutionary rates vary among branches in the phylogeny but that this variation can be described using only a few discrete rates. In many cases, this would be considered a reasonable assumption because we expect closely related species to evolve at similar rates. As a result of common ancestry, species tend to share many biological features with their relatives, including heritable traits that influence rates of evolution. Local-clock methods permit different molecular clocks to exist in different groups of organisms. For example, one might distinguish between rates in baleen whales (mysticetes) and toothed whales (odontocetes), because the latter tend to evolve much more rapidly (Dornburg et al. 2012).

Local-clock methods retain some of the advantages of a strict molecular clock, without the restrictive assumption of a single rate of evolution across all lineages. However, there are significant difficulties in implementing local-clock methods, particularly in choosing the number of local clocks and determining how they are assigned among the species being studied. Recently, methods have been developed to conduct some of these steps objectively (Drummond and Suchard 2010; Paradis 2013), but their performance has not yet been examined comprehensively.

Rate-Smoothing Methods

Given that the rate of evolution is likely to be influenced by heritable traits, we can also treat the rate as a biological character that evolves over time (Gillespie 1991). Consequently, we would expect rates to be similar, but not necessarily identical, between neighboring branches in the phylogeny.

One way of putting this assumption into practice is to penalize large changes in rates between neighboring branches. A number of such “rate-smoothing” methods have been developed, including nonparametric rate-smoothing (Sanderson 1997) and penalized likelihood (Sanderson 2002).

The nonparametric rate-smoothing method operates by minimizing an objective function based on the sum of rate changes between branches in the phylogeny (Sanderson 1997). In penalized likelihood, rate changes between branches incur a penalty (Sanderson 2002). The weight of this penalty is governed by a smoothing parameter, the value of which can be optimized objectively. Both of these methods assume that the phylogeny is known or has been estimated reliably.

Bayesian Relaxed Clocks

Some relaxed-clock methods use an explicit model of rate variation among branches. These models are statistical rather than mechanistic, in that they model rate variation without making any statements about the causes of this variation. Relaxed-clock models tend to be parameter rich and have been implemented in Bayesian methods for phylogenetic analysis. The models of rate change can be broadly divided into two classes, based on whether evolutionary rates are assumed to be correlated between related lineages (Ho 2009).

In autocorrelated models of rate change, the rate is assumed to “evolve” gradually along branches of the tree (Thorne et al. 1998; Aris-Brosou and Yang 2002). The rate along a descendent branch is drawn from a distribution centered on the rate in its ancestral branch. As a consequence, neighboring branches are likely to have similar evolutionary rates. Various parametric distributions have been used in autocorrelated models of rate change, including lognormal and exponential distributions. The statistical properties of some of these models have been questioned (Welch et al. 2005; Lepage et al. 2006).

In uncorrelated models of rate change, the rate along each branch in the phylogeny bears no a priori similarity to the rates along its neighboring branches (Drummond et al. 2006). However, the rates across the tree are drawn from a single underlying distribution, such as a lognormal, exponential, or gamma distribution.

Models of autocorrelated and uncorrelated rates are probably applicable to different data sets (Ho 2009). When comparing closely related species, much of the rate variation among lineages can probably be explained by differences in biological characteristics. When the analysis involves distantly related organisms, however, it is possible that traces of rate autocorrelation break down. Various statistical methods can be used to choose the best-fitting model of rate variation among lineages for a given data set (Baele et al. 2013; Paradis 2013).

Conclusions

Relaxed molecular clocks make it possible to estimate evolutionary rates and timescales from genetic data even when rates vary among lineages. Various relaxed-clock methods have been developed, with statistical models designed to capture and account for heterogeneity in evolutionary rates. In view of the growing understanding of the factors driving variation in molecular rates, the next step is to incorporate biological knowledge into models of rate variation.

Cross-References

- ▶ [Amino Acid](#)
- ▶ [Gene Sequencing](#)
- ▶ [Molecular Clocks](#)
- ▶ [Molecular Clock Calibrations](#)
- ▶ [Molecular Dating of Evolutionary Events](#)
- ▶ [Molecular Rate Variation \(Molecular Clocks\)](#)
- ▶ [Polymerase Chain Reaction DNA Amplification](#)

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Minerals, (^{40}Ar - ^{39}Ar)

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Definition

Dating potassium-bearing minerals using the ^{40}Ar - ^{39}Ar technique is the most popular approach to determining the rates and timescales of geological processes across a wide range of geological time and is applied to dating igneous, sedimentary, and metamorphic rocks including meteorites and Moon rocks. Dating minerals using the Ar-Ar dating method is performed on purified mineral separates, individual mineral grains, and in situ in thick polished slabs.

Introduction

The earliest Ar-Ar dating studies were analyses of whole rock samples to investigate the age of meteorites and the first Moon rocks returned by the Apollo 11 astronauts (e.g., Turner et al. 1966, 1971). Terrestrial studies quickly applied the new dating techniques to mineral separates (e.g., Lanphere and Dalrymple 1971). Whole rock dates using the Ar-Ar technique are used predominantly for volcanic rocks where they can distinguish between instantaneous eruption ages and those disturbed by alteration of additional excess argon. Whole rock Ar-Ar dates of basalt eruptions are in fact dominated by potassium in the glass phase (potassium is incompatible in the main mineral phases pyroxene, olivine, and plagioclase). Unfortunately glass is also commonly altered to clay minerals, some of which yield ages reflecting the later fluid flow events (e.g., illite) and some do not retain argon quantitatively (e.g., smectite). Moreover argon is more soluble in melt than minerals so glass can exhibit anomalously old ages caused by excess argon. So even in this scenario, understanding mineral Ar-Ar dates can be important.

Mineral dates have been measured for both K-Ar and Ar-Ar dating because of their versatility. For example, muscovite mineral ages have been used to date high-level igneous intrusions, metamorphic cooling, and sediment provenance, and alkali feldspars have been used to date mega-eruptions and metamorphic thermal histories.

Criteria for Successful Mineral Ar-Ar Dating

The fundamental reason for mineral dating is that the ages can be interpreted in terms of geological processes including crystallization and cooling. While some ages yield simple ages of instantaneous events, others yield additional information on cooling patterns and fluid flow. There are several important mineral- and rock-specific parameters that should be considered in order to interpret the ages:

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- *Mineral characterization and analytical approach*: Ensuring mineral separate purity is an essential prerequisite for mineral Ar-Ar dating; in short you have to know what you're dating in order to interpret the age. Mineral identification is normally undertaken optically using thin sections, often combined with elemental composition measured using electron microprobe. Several techniques are commonly used to measure mineral Ar-Ar ages including stepped heating mineral separates of 10–100 mg and laser heating of mineral separates commonly less than 1 mg or as single grains (see “► [Single Crystal Laser Fusion \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”; McDougall and Harrison 1999; Kelley 2002a). In addition, Ar-Ar age variations within individual minerals can be measured using laser ablation (pits 25–200 μm diameter) to extract argon from individual laser pits in mineral grains in rock sections or separately (see “► [Structural Fabrics, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”; Kelley et al. 1994).

The potassium content and age of minerals are the two key parameters in determining the analytical approach. Higher potassium and older ages make analysis of smaller samples possible. Such samples can usefully be analyzed using UV laser to extract additional temporal and thermal information (e.g., Flude et al. 2013). High-potassium minerals are more commonly dated, but precise and geologically meaningful ages can be measured on minerals with low potassium content (e.g., Renne et al. 1997). In contrast Ar-Ar mineral dating of young volcanic rocks requires multiple grains analyzed as a pure mineral separate (e.g., Ton-That et al. 2001). Greater care is essential in dating all minerals since contamination is more likely to cause problems of interpretation. For example, a young volcanic rock can be dated using plagioclase, but it has become a common practice to briefly etch the grains using acid such as HF to remove any adhering glass or clay minerals because glass is more likely to contain high potassium contents and excess argon (e.g., Esser et al. 1997), and clay minerals may also contain significant potassium and younger ages.

What do mineral ages mean – closure and other models: The key property of mineral is that the ages they yield can be interpreted as a single geological event or a process such as cooling. Only in the case of geologically instantaneous volcanic eruption and cooling do all minerals in a rock yield a single age. When rocks cool more slowly or recrystallize, minerals yield different ages.

The capacity of mineral Ar-Ar dating to date a range of different types of event is the result of differing argon retention properties. Argon is a gas and diffuses through minerals at high temperature, but diffusion rates slow down at lower temperatures. The relationship between diffusion rate and temperature is exponential, so small changes in temperature cause rapid changes in diffusion rate. Considered over geological time, this diffusion rate change can approach a switch-like behavior and the point at which the Ar-Ar clock starts. Dodson (1973) formulated a mathematical solution to this process which made simplifying assumptions but proved to be very powerful tool in quantifying link between thermal closure and age that all later studies followed. The “closure temperature” concept (Dodson 1973) has been central to the popularity of mineral Ar-Ar dating because it provides both time and temperature simultaneously.

The early literature on closure temperatures is characterized by empirical closure temperatures for minerals; for example, biotite closure was considered to be around 300 °C, and most mineral closure temperatures are in geological useful range from around 150 °C to 500 °C. However, reliable experimental argon diffusion data is now available for all common potassium-bearing minerals, so mineral closure should always be calculated using the mineral-specific diffusion parameters (e.g., Baxter 2010), estimated grain size, and cooling rate. While the Dodson (1973) formula was a good estimate for simple cooling, many recent studies use a finite difference model (e.g., Wheeler 1996) both for whole-grain ages and within grain age variation. This type of model is capable of simulating the coupled loss of argon with varying temperature history, and coupled radiogenic production of

^{40}Ar , and has enabled a better understanding of metamorphic ages (e.g., Warren et al. 2012) including partial argon retention of Ar-Ar ages in high-pressure micas cycled through rapid orogenic burial and exhumation.

Another extension of closure temperature is the use of diffusion data derived from stepped or cycled heating of complex alkali feldspar mineral grains from granites and basement metamorphic rocks (e.g., Harrison and Lovera 2013). This approach has produced thermal histories from many individual mineral samples, although the interpretation has sometimes been controversial (e.g., Parsons et al. 1999).

- Not all mineral Ar-Ar ages can be interpreted in terms of closure due to slowing argon diffusion with temperature. In conditions close to the closure temperature, argon loss can also be controlled by deformation, grain-size reduction, and recrystallization (e.g., see “► [Structural Fabrics, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”). Fluids play a key role in recrystallization and mineral growth and some metamorphic mineral Ar-Ar ages, particularly amphiboles (e.g., Villa et al. 2000) and low-temperature K-feldspar (e.g., Mark et al. 2007).

Argon solubility, excess argon, and mineral Ar-Ar ages: One of the basic assumptions of Ar-Ar dating is that the mineral contains negligible amounts of ^{40}Ar at the point of closure. However, this assumption is “at odds” with experimental noble gas research which indicates that partition coefficients are not zero (e.g., Chamorro et al. 2002). Non-zero argon partition coefficients in turn imply that all minerals that reach equilibrium with silicate melt or hydrous liquid acquire low concentrations of non-atmospheric argon contamination. This conclusion appears to be a fundamental challenge to Ar-Ar mineral dating success, and yet most measurements yield geologically meaningful ages – so why is this?

There are some geological circumstances where Ar-Ar dating works less well and minerals yield anomalous ages caused by high concentrations of radiogenic argon not related to in situ potassium decay (Note that $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of metamorphic fluids are never the same as the Earth’s atmosphere and commonly very high). There are two scenarios in which this can affect the mineral Ar-Ar age, which can be described as fluid present or open system and fluid absent or closed system (Kelley 2002b). In the fluid present system, high concentrations of excess argon in the fluid (melt or hydrous) lead to partition into the mineral or incorporation in a crystallizing mineral. In the fluid absent case, the lack of any fluid means that the minerals become the main reservoir for argon despite the temperatures exceeding those normally associated with closure (e.g., Kelley and Wartho 2000).

Recent work has helped to characterize these scenarios since argon solubility has been measured experimentally in hydrous liquids including sea water (summarized in Kelley 2002), and in silicate melts at high temperature (e.g., Carroll and Stolper 1993), and is in the range ~10–100 ppm for hydrous liquids and ~0.1–1 ppm for silicate melts. Experimental data has now revealed a reproducible pattern of solubility (Brooker et al. 2003; Heber et al. 2007) and discovered significant variations between mineral types (e.g., Jackson et al. 2013). Excess argon should thus be understood in terms of variable solubility and partition, in the same way as other trace elements are understood to partition between minerals.

Minerals Used for Ar-Ar Dating

- Minerals of several classes are used for mineral Ar-Ar dating, some more commonly than others. Orthosilicates have rarely been used for Ar-Ar dating and had a reputation for excess argon, but it

seems this was ill founded and mainly the result of their low potassium contents (100 s of ppm). There are several records of successful pyroxene dates in meteorites and recent work has shown that they can yield useful ages and argon diffusion rates in terrestrial rocks (Cassata et al. 2011). Framework silicates are very commonly dated, particularly alkali feldspars in igneous rocks where sanidine has yielded some of the youngest reliable Ar-Ar ages including the eruption of Vesuvius in AD 79 (Renne et al. 1997). Alkali feldspars have also been used in granites and basement rocks to date cooling and yield thermal histories (e.g., Harrison and Lovera 2013). Plagioclase is also a very commonly dated mineral, although the low potassium contents (0.05–1.0 wt%) make sample purity essential. Feldspathoids (up to 14 wt%) and anorthoclase (3–4 wt%) also yield reproducible ages but are less common. Chain silicates (amphiboles) are commonly dated, although they generally have lower potassium contents (generally 0.05–1.5 wt%). Sheet silicates including biotite, phlogopite, muscovite, and phengite (6–9 wt %) are all common mineral targets for Ar-Ar dating. Finally, clay minerals have also been dated using the Ar-Ar technique and illite is perhaps the most commonly used since it has similar potassium content to muscovite. Clay mineral dating using the Ar-Ar technique involves particular challenges caused by the recoil of ^{39}Ar during the irradiation process, although this has been successfully overcome by encapsulating pure clay mineral separates (see “► [K-Ar/ \$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ Dating](#)” and “► [Clays and Glauconites, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”).

Interpretation of Mineral Ar-Ar Dates

Mineral ages from igneous rocks: Mineral ages from lavas and volcanic deposits (i.e., tuff and tephra layers) provide chronostratigraphic markers that represent geologically instantaneous events, which are routinely used to calibrate the geological timescale (e.g., Kuiper et al. 2008; Rivera et al. 2011; Storey et al. 2012) and date paleomagnetic events, such as polarity reversals (e.g., Deino et al. 2002). Mineral ages are also used to assess the impact of explosive volcanic eruptions (e.g., Ton-That et al. 2001), correlate stratigraphy and biostratigraphy over large areas, and place an age upon and hominid activities (e.g., Deino and Potts 1992; Storey et al. 2012). High-temperature alkali feldspars, in particular sanidine, appear to be less susceptible to both xenocrystic contamination and excess argon and are readily used in Ar-Ar geochronology to determine the timing of volcanic eruption. Plagioclase is commonly used for dating basaltic igneous rocks where it is often the only K-bearing phase available (e.g., Renne et al. 1995), although their low K contents do mean that the incorporation of inherited and/or excess ^{40}Ar can cause significant increases to Ar-Ar apparent age determinations. Plutonic rocks are also dated using mineral Ar-Ar dates most commonly using micas or amphiboles since the lower-temperature feldspars yield cooling rather than crystallization ages, but even these minerals can yield ages significantly younger than U-Pb ages on minerals from the same intrusion.

Mineral ages from metamorphic rocks: Mineral Ar-Ar ages from metamorphic rocks provide key information on both time and temperature during cooling or crystallization as discussed above. Sequences of mineral ages such as muscovite, biotite, and alkali feldspar can yield extended portions of thermal history in some cases. However mineral Ar-Ar dates can also be complicated by processes that alter the Ar concentration both during and after crystallization (see “► [Metamorphic Terranes, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”). Measured mineral Ar-Ar ages may therefore relate to the timing of mineral crystallization and recrystallization, cooling following crystallization, and deformation with associated recrystallization. Careful petrographical observations allow the relative timing of (re)crystallization and/or deformation and the pressure-temperature history following crystallization to be estimated.

Geochronological data from other decay systems, such as U-Pb where “age” and metamorphic “stage” can clearly be linked, are useful for providing a solid framework in which to interpret the Ar-Ar data. In situ laser ablation methods allow Ar-Ar ages within grains to be measured to determine whether ages may be linked to changes in chemical composition, textural position, grain size, or regions of grain deformation (see “► [Structural Fabrics, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”). Numerical modeling provides constraints on the expected ages for different grain sizes at different cooling/decompression rates in cases where an open grain boundary network may be assumed (e.g., Warren et al. 2012). In all cases the relative petrographical framework and geochronological constraints from other systems can be used to determine whether mineral grains degassed efficiently at high temperatures or whether they might contain additional or “excess Ar” sourced from a precursor K-bearing mineral, a neighboring K-bearing mineral in a closed system where fluid absence prevented its escape, or alternatively argon in a concentrated fluid in which the mineral was crystallizing.

Sedimentary rocks: Mineral Ar-Ar ages provide two important types of information, detrital mineral ages from clastic rocks (often muscovite but also occasionally alkali feldspar and biotite) and ages for newly grown low-temperature minerals including clays (see “► [Clays and Glauconites, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”) and authigenic alkali feldspar. Ar-Ar ages for detrital minerals became popular when techniques were developed for analyzing individual grains (e.g., Kelley and Bluck 1992). Bulk ages were only ever useful as general indicators, whereas dating individual mineral grains enabled comparison not only of the time lag between cooling/erosion and deposition but also age variations within individual samples. This capability has been exploited to understand mountain building and erosion processes including recycling (e.g., Sherlock 2001; Najman et al. 2001) and determining glacial source regions (e.g., Hemming and Hajdas 2003; Reynolds et al. 2004). Mineral Ar-Ar ages for authigenic minerals are less common mainly because of the issues of obtaining pure separates and recoil effects upon the submicron grains (see “► [Clays and Glauconites, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)”). However other authigenic minerals are known to yield meaningful ages. Alkali feldspar overgrowths have been successfully dated using UV laser ablation (e.g., Mark et al. 2007) and can indicate both authigenesis and multiple fluid flow events (e.g., Sherlock et al. 2005). Gangue minerals such as cryptomelane have also been successfully dated (Vasconcelos et al. 1992).

Cross-References

- [Clays and Glauconites, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)
- [K-Ar/ \$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ Dating](#)
- [Metamorphic Terranes, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)
- [Single Crystal Laser Fusion \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)
- [Structural Fabrics, \(\$^{40}\text{Ar}\$ - \$^{39}\text{Ar}\$ \)](#)

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Jack Hills Zircon

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Definition

The Jack Hills are located ~800 km north of Perth, Western Australia, within the Archean Narryer Terrane. They became internationally known as the site of the world's oldest crystals (Compston and Pidgeon 1986; Wilde et al. 2001; Mojzsis et al. 2001).

Initial investigation at Mt. Narryer (~50 km southwest of Jack Hills) led to the discovery of a granulite-facies quartzite containing detrital zircons with an age ~4,150 Ma (Froude et al. 1983). Subsequent work on a greenschist facies conglomerate from Jack Hills (W74 site on Eranondoo Hill) led to the identification of two even older zircon grains with ages of $4,276 \pm 12$ Ma (Compston and Pidgeon 1986). A reinvestigation of zircons from that site identified one grain that recorded a $^{207}\text{Pb}/^{206}\text{Pb}$ age of $4,404 \pm 8$ Ma (Wilde et al. 2001), the oldest age obtained from terrestrial material.

Jack Hills' zircons have continued to provide important information on the early Earth. This has included oxygen, lithium, and lutetium-hafnium isotopic data and titanium-in-zircon thermometry, as well as studies at the atomic level on lead distribution. Initial studies of oxygen isotopes identified elevated $\delta^{18}\text{O}$ values, implying zircon growth in rocks previously subjected to interaction with surface waters (Wilde et al. 2001; Mojzsis et al. 2001), leading to the hypothesis of a cool early Earth (Valley et al. 2002).

More controversial is whether the oxygen data require the presence of oceans and continents in the Hadean and whether plate tectonics was operative at this time (Hopkins et al. 2008). This is compounded by the lack of direct evidence on the nature of the protolith of the ancient detrital zircons. However, lutetium-hafnium data are consistent with the protolith being an intermediate to mafic igneous rock, with the possibility that it was formed from consolidation of a magma ocean at ~4.45 Ga (Kemp et al. 2010).

Cross-References

- ▶ [Acasta Gneiss](#)
- ▶ [Age of the Earth](#)
- ▶ [Lutetium-Hafnium Dating](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)
- ▶ [Zircon](#)

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Uranium Series, Ice

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Definition

Use of intermediate decay products within the ^{238}U or ^{235}U radioactive decay chains to evaluate the age or history of glacial ice and ground ice in permafrost.

Introduction

Uranium-series isotope disequilibrium effects provide a means of dating ice in terrestrial environments where mineral particles entrained in ice produce recoil-derived isotopes that are redistributed into the interstitial ice. Detectable recoil-driven disequilibrium in activity ratios of ^{234}U and ^{238}U , here indicated as ($^{234}\text{U}/^{238}\text{U}$), occurs over timescales of 10^3 – 10^6 years and has been extensively observed in natural waters as a function of water–rock contact (see, e.g., Bourdon et al. 2003; Porcelli and Swarzenski 2003). In a few studies, recoil effects have been used to derive age information for ice, based on mineral–ice contact in permafrost and ice cores of sufficient age (Ewing et al. Unpublished data; Fireman 1986; Goldstein et al. 2004; Aciego et al. 2011). Given the growing need for alternative dating techniques to reliably link paleoenvironmental records for the cryosphere over long timescales ($>20,000$ years), particularly in discontinuous frozen cores (Goldstein et al. 2004), it is probable that U-series applications in cryospheric environments will continue to receive attention. Moreover, waters mobilized by thawing ice with inherited U-series disequilibrium may provide a metric for hydrologic outcomes of a warming climate (Kraemer and Brabets 2012), if the extent and duration of mineral–ice contact is known.

Age Equation

When mineral particles at or near secular equilibrium are suspended in ice for sufficient time, disequilibrium of parent–daughter pairs within U-series decay chains occurs as a function of alpha-recoil loss from the mineral particle surfaces into the ice and alpha decay within the ice (Fig. 1). This recoil-driven disequilibrium can be used to derive age information for the ice based on activity ratios (A) of the parent–daughter pair in ice (A_{ice}) and initial water (A_{initial}), the fraction of mineral material subject to recoil loss (f_{α}), and the distribution of U between solids and thaw water (R_s). If a closed system is assumed, the age of the ice (t_{ice}) can be expressed in terms of activity ratios as (Fireman 1986; Aciego et al. 2011):

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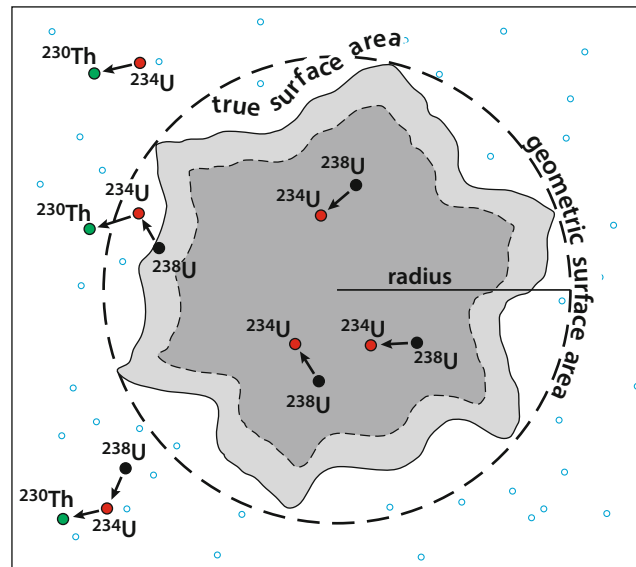


Fig. 1 Schematic of recoil accumulation of ^{234}U daughters in ice from a dust particle with surface roughness that increases the recoil fraction relative to the geometric surface area predicted for a smooth surface (Aciego et al. 2011; used with permission). Weathering rinds may alter surface roughness and change mineral-fluid evolution over time (Andersen et al. 2007; Pelt et al. 2008)

$$t_{\text{ice}} = -\left(\frac{1}{\lambda_{234}}\right) \ln \left[\frac{A_{\text{ice}} - f_{\alpha} R_s - 1}{A_{\text{initial}} - f_{\alpha} R_s - 1} \right] \quad (1)$$

where λ_{234} is the decay constant for ^{234}U and R_s is the ratio of ^{238}U in the solid to ^{238}U in the ice. An example of the evolution of $(^{234}\text{U}/^{238}\text{U})$ values in ice simulated over time using an appropriate range of f_{α} and R_s values can be seen in Fig. 2, with reference to observed values in permafrost.

Ice Cores

A key study in the development of U-series as an indicator of ice age focused on ice from the Allan Hills area of Antarctica (Fireman 1986), where dusty ice samples were observed to contain ^{222}Rn in proportion to dust content. Longer-lived U-series isotopes were then examined in order to date the ice based on its dust content. Activities of ^{226}Rn , ^{230}Th , and ^{234}U were used to obtain a date of $210\text{--}330 \times 10^3$ years for the ice based on a presumed recoil fraction (f_{α}) of 0.25; however, subsequent work has argued for younger ages (30,000 years) based on improved leaching techniques and inheritance from precipitation ($(^{234}\text{U}/^{238}\text{U})_{\text{initial}} = 1.4$) (Goldstein et al. 2004). More recently, $(^{234}\text{U}/^{238}\text{U})$ values were evaluated for samples from the EPICA (European Project for Ice Coring in Antarctica) Dome C ice core (Aciego et al. 2011), resulting in model ages of $83\text{--}870 \times 10^3$ years for sections within the $\sim 3,200$ m core, based on micro-BET measurements and consideration of a fractal dimension to compute recoil fractions ($f_{\alpha} = 0.14\text{--}0.22$), as well as an assumed initial $(^{234}\text{U}/^{238}\text{U})$ of 1.14. In this analysis, $(^{234}\text{U}/^{238}\text{U})$ values increased with depth as expected for ice core, and derived ages were consistent with other measures of age in the core, although uncertainties were $\sim 25\text{--} > 50\%$ due to uncertainty in recoil fractions (f_{α}) and uranium distributions (R_s).

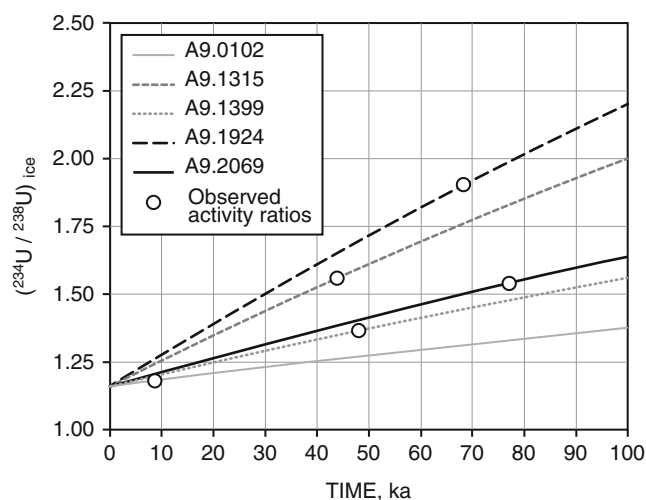


Fig. 2 Evolution of $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ values in central Alaska permafrost samples from borehole A9 at depths of 102–2,069 cm (indicated in sample number), assuming a starting value in precipitation of 1.161 (Ewing et al. [unpublished data](#)). Values increase with depth (time) as expected for syngenetic permafrost (French and Shur 2010) and are consistent with ice-core depth trends (Aciego et al. 2011). Curves represent modeled activity ratios over time in ice, derived using Eq. (1), and the observed $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ values at the indicated depths in cm, the appropriate combinations of recoil fraction based on BET surface area ($f_{\alpha} = 0.11\text{--}0.23$), and a fitted ratio of U concentrations in the mineral particles versus ice ($R_s = 5.7\text{--}32.3$) based on a leaching experiment. Variation in values of f_{α} and R_s explains variability in the degree of increase in activity ratios with depth (corresponding to time). Calibration of the $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ -derived age model was provided by an analysis of dissolved organic carbon in the sample at 102 cm (A9.0102), which had a radiocarbon age of 8,100 years

Permafrost

Evidence of elevated $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ values in thawing permafrost has been inferred from surface water data (Kraemer and Brabets 2012; Koch et al. 2013) and measured directly in syngenetic (ice-rich) loess permafrost cores from central Alaska (Fig. 2; Ewing et al. [Unpublished data](#); Koch et al. 2013). In the permafrost core study (Ewing et al. [Unpublished data](#)), model ages of $\sim 2,000\text{--}80,000$ years were derived from $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ values in sections of core obtained from 0.8 to 20 m depth. The observed $(^{234}\text{U}/^{238}\text{U})_{\text{ice}}$ values increased with depth in multiple cores, consistent with expectations based on syngenetic permafrost formation through upward propagation of permafrost with concurrent loess deposition. Modeled age results were based on R_s values of 5–18 derived from a leaching experiment on five samples and f_{α} values of 0.11–0.23 derived from BET measurements in five samples with organic matter removed (assuming no fractal effect in calculation of recoil fractions). As observed for Antarctic ice cores, uncertainties in the analysis of permafrost samples were also substantial (up to an order of magnitude), reflecting the need for improved assessment of surface area, secondary phases, and U distribution.

An important distinction from ice cores is that syngenetic loess permafrost has mineral contents of $\sim 50\%$ by volume, or roughly 700 mg of loess per kg of total sample, whereas even dusty ice core has on the order of 1 mg dust per kg sample, resulting in lower mineral surface area on a sample volume basis and much lower U abundance throughout. Additionally in permafrost, the starting value of precipitation may be less easily inferred than in continuous ice core due to active layer freeze–thaw dynamics (Ewing et al. [Unpublished data](#); French and Shur 2010).

Complications

Several complications in the assessment of ice age using U-series isotopes merit further study. The first is the starting value of precipitation, which can dramatically affect model age values (Goldstein et al. 2004). Second, the recoil fraction (f_r) is a function of surface area and recoil distance, with complications related to the scale of surface roughness and particle shape, such that mathematical derivation from BET measurements is needed (Bourdon et al. 2009; Aciego et al. 2011). Moreover, the measurement of BET in very small dust samples within ice cores poses challenges, but has been addressed in one study (Aciego et al. 2011). A third key complication arises where liquid water is present due to abundant mineral surface area in relatively shallow permafrost environments, and weathering rinds may develop on particle surfaces over time, altering surface roughness (Andersen et al. 2007; Pelt et al. 2008). Finally, the separation of ice from mineral phases for analysis can be challenging, and buffered solutions (e.g., EDTA, ammonium) have been used to prevent redistribution of U-series elements during separation as a result of their geochemical character (Goldstein et al. 2004; Aciego et al. 2009, 2011).

Summary

The validity of dating ice with U-series model ages has been demonstrated, but with substantial uncertainty derived from difficulties in measuring surface area and U distribution. Complementary dating methods are needed to corroborate this approach in permafrost and ice core studies. Nevertheless, field and stratigraphic evidence suggests that ground ice can be preserved for hundreds of thousands of years despite large changes in climate over that time span (Froese et al. 2008; Reyes et al. 2010). Consequently, it is likely that application of U-series age models for ice in conjunction with other dating tools (radiocarbon, luminescence, amino-acid racemization) will continue to be investigated in cryosphere environments. Moreover, chronological constraint of ice-preserved paleoecological histories continues to be an important area of climate-change investigation and may benefit from age evaluation based on U-series isotopes in ice cores.

Cross-References

- ▶ [Amino Acid Racemization, Loess and Glacial Sediments \(AAR\)](#)
- ▶ [Aquifer Characteristics \(U-Series\)](#)
- ▶ [Chemical Weathering \(U-Series\)](#)
- ▶ [Ice Cores](#)
- ▶ [Luminescence, Loess](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [U-Series Dating](#)

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Luminescence, Geomorphological Processes

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Definition

Geomorphology is the science that studies the origin and development of landforms and how those landforms combine to form landscapes. Landforms are shaped by *geomorphological processes*, many of which involve the weathering, erosion, transportation, and deposition of surface materials (rock, sediment) by gravity, ice, wind, or water. Both erosional and depositional landforms can be identified, and study objectives may include establishing (1) the initial timing of surface material movement (hence, landform age), (2) the timings of subsequent surface material movement (hence, landform development rate), and (3) the nature of surface material movement (sediment dynamics). Using a similar threefold breakdown, the focus here is on how *luminescence dating* can contribute to these objectives. Luminescence dating is a family of techniques most suitable for investigating fine-grained (typically silt, sand) depositional landforms. The basic principles of luminescence dating and the various techniques are explained in other entries (e.g., see “► [Luminescence Dating](#)”), and the emphasis here is mainly on optically stimulated luminescence (OSL) dating, which typically can be applied to quartz-rich sediment ranging in age from a few years to several hundred thousand years.

Principal Applications of Luminescence Dating in Geomorphology

Luminescence dating relies on the exposure of transported sediment to light prior to deposition and burial of that sediment. Consequently, OSL and other luminescence techniques are best suited to the investigation of depositional landforms originating and/or developing as a result of one or more of the following processes, all of which involve varying degrees of sediment exposure to light: aeolian (e.g., loess sheets, dunes), colluvial (e.g., aprons, glacis), fluvial (e.g., alluvial fans, river terraces), and wave and tidal action (e.g., beach ridges, spits). Luminescence techniques have been less widely applied to the investigation of glacial, deeper marine, tectonic and volcanic processes because of reduced exposure of sediment to light and/or less suitable (coarser or finer) grain sizes or minerals, although techniques are being developed to cater for these issues (see “► [Luminescence, Deep Sea Marine and Lacustrine](#)”, “► [Luminescence, Glacial Sediments](#)”, “► [Luminescence, Earthquake and Tectonic Activity](#)”). Numerous recent reviews have outlined the applications of luminescence dating in specific areas of geomorphological research (e.g., Duller 2004; Singhvi and Porat 2008; Fuchs and Lang 2009; Cunningham and Wallinga 2012), and the following provides only a brief outline of three main, possibly interrelated, applications.

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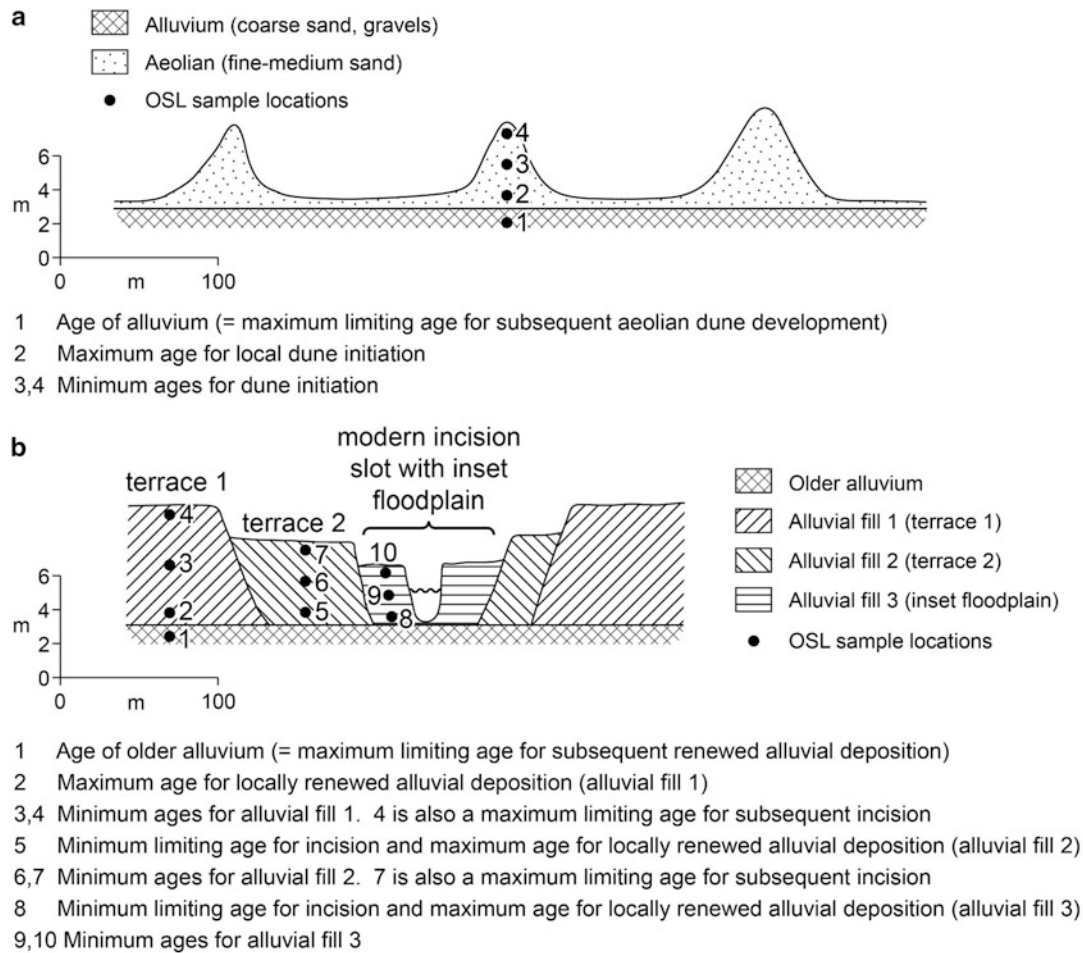


Fig. 1 Examples of possible strategies for luminescence sample collection and the insights into geomorphological processes and landform dynamics that may result: **(a)** Cross-sectional view of aeolian linear dunes **(b)** Cross-sectional view of an incised river and flanking alluvial deposits

The Initial Timing of Sediment Deposition

Commonly, luminescence dating is used to establish the initial timing of sediment deposition, thereby providing information on landform age. Examples include OSL dating of the timing of aeolian deposition in deserts (e.g., Hollands et al. 2006); in such instances, the ages for the basal aeolian sediments provide *maximum* ages for the overlying dune landforms (Fig. 1a). Similarly, luminescence dating of basal sediment can help establish the maximum ages of a variety of other landforms including colluvial aprons (e.g., Botha et al. 1994), lacustrine beach ridges (e.g., Nanson et al. 1998), and river floodplains and terraces (e.g., Keen-Zebert et al. 2013). In addition, dating of the initial timings of deposition in adjacent landforms may be used to provide bracketing ages for geomorphological processes that partly involve erosion; for example, the timing of river incision can be bracketed by establishing an age for the alluvial sediments into which a river has incised, and an age for the sediments subsequently deposited within the incision slot (Fig. 1b). The former provides a maximum limiting age for incision and the latter a minimum limiting age for incision, thereby bracketing the actual timing of incision (e.g., Keen-Zebert et al. 2013).

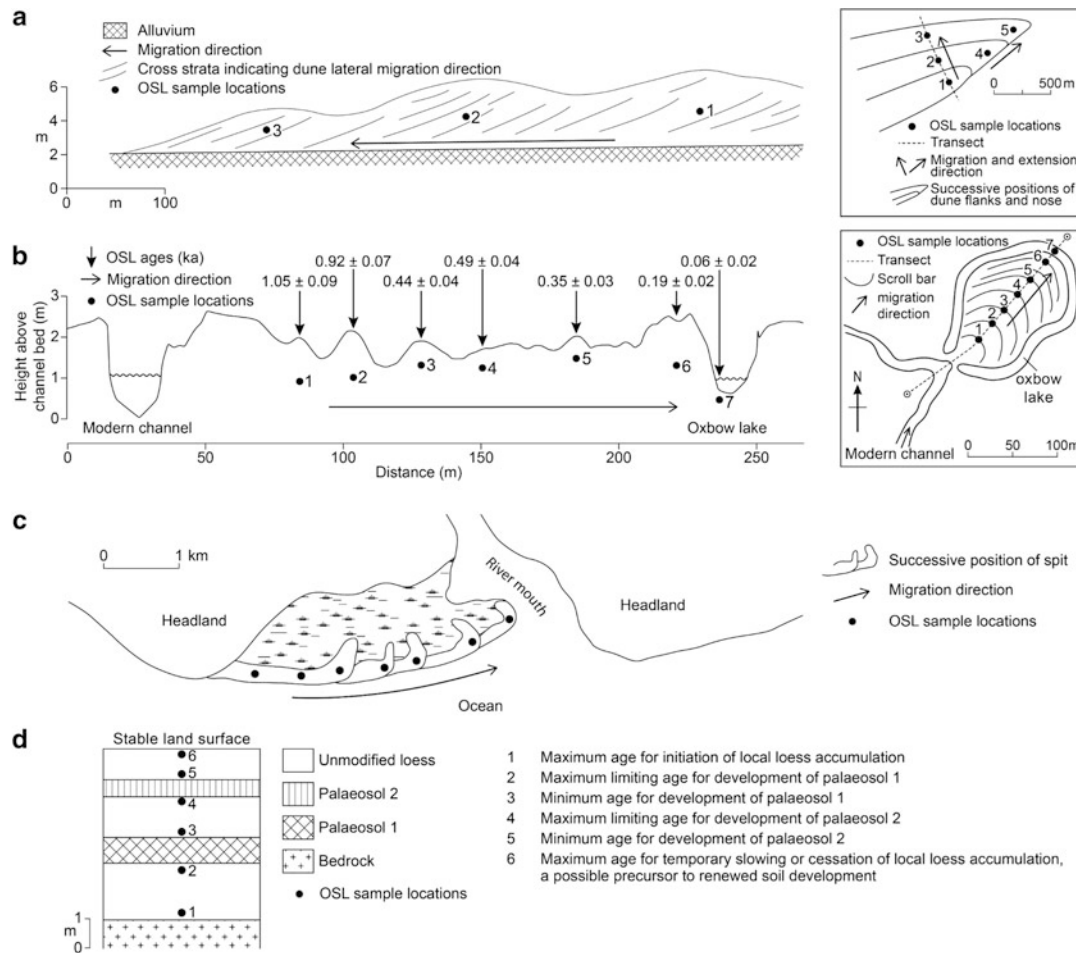


Fig. 2 Examples of possible strategies for luminescence sample collection where the focus is on establishing landform development rates: **(a)** Cross-sectional and plan view of a laterally migrating and longitudinally extending aeolian linear dune **(b)** Cross-sectional and plan view of a laterally migrating meander, with scroll bars formed on the inside bend. OSL ages for scroll bars and the oxbow lake infill are derived from Rodnight et al. (2005) and Tooth et al. (2009) **(c)** Plan view of a prograding coastal spit and back barrier complex **(d)** Side view of a vertically accumulated loess-paleosol succession

The Timings of Subsequent Sediment Deposition

Typically, establishment of the initial timing of deposition is coupled with the investigation of the timings of subsequent deposition, thereby providing information on landform development rate. Examples include using multiple luminescence ages from sediment bodies to establish vertical accretion rates (Fig. 1), but sampling strategies also can be designed to establish dune lateral migration and/or forward extension rates (Fig. 2a), meander bend growth rates (Fig. 2b), or coastal progradation rates (Fig. 2c) (e.g., Bristow et al. 2005; Rodnight et al. 2005; Hollands et al. 2006; Roberts and Plater 2007; Rink and López 2010; Telfer 2011). In cases where single or multiple bracketing ages for river incision can be established (e.g., across a flight of alluvial terraces), these can be coupled with the depth of incision to provide a mean long-term incision rate (Fig. 1b). Establishing OSL ages for relatively unmodified sediments above and below paleosols can also help to bracket soil formation rates (Fig. 2d), as has been demonstrated in studies of loess, aeolian dunes, and sand ramps (e.g., Roberts 2008; Fujioka et al. 2009; Telfer et al. 2012).

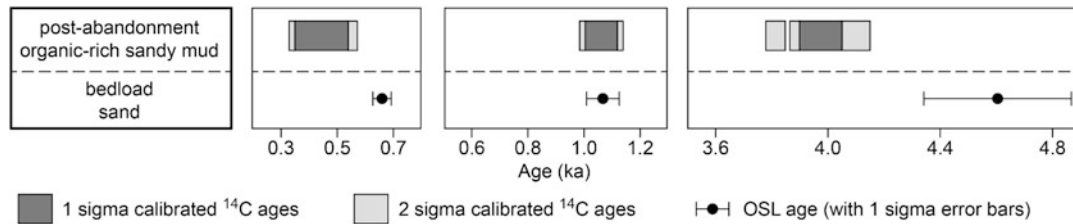


Fig. 3 Schematic comparison between OSL ages for bedload sand in paleochannels of the Klip River, South Africa, and the generally younger ^{14}C ages for overlying organic-rich sandy muds (modified from Rodnight et al. 2006)

The Nature of Sediment Movement

Some recent applications of luminescence techniques have focused less on the timing and rates of landform development and more on sediment dynamics. For instance, OSL dating has been used in combination with hydraulic modelling to provide fundamental insights into the nature of storage and flushing of fine-grained matrix sediments in small mountain streams in southeast Australia (Thompson et al. 2007), and investigations of downstream quartz sensitivity (brightness) change in larger, lower gradient Australian rivers potentially may provide information on river style and associated fluvial processes, including bedload transport rate, and water depth and turbidity (Pietsch et al. 2008). In other geomorphological contexts, a variety of analytical approaches have been employed to investigate other aspects of local sediment dynamics, including bioturbation and its implications for depositional stratigraphy and luminescence chronologies (Bateman et al. 2007).

Key Issues in Applications of Luminescence Dating in Geomorphology

The following outlines some overarching considerations that arise from applications of luminescence dating in geomorphology.

Sampling Design and Age Consistency

Careful sampling designs can help to provide an internal check on luminescence age consistency. For instance, luminescence ages for the underlying sediments upon which the basal aeolian or fluvial sediments have been deposited provide a *maximum* limiting age for subsequent development of the dune or floodplain and clearly should be older than the maximum ages established by dating of the basal aeolian or fluvial sediments underlying the landform of interest (Fig. 1). In addition, where several samples have been collected in vertical, lateral, or longitudinal sequence within or across landforms, normal stratigraphic principles apply; the luminescence ages for sediment that is superimposed upon, laterally adjacent to, or cross-cutting pre-existing sediment should be younger than the ages for the preexisting sediment (Fig. 2b).

Comparison with Independent Geochronometers

Confidence in the veracity of luminescence ages also can be provided by comparisons between different luminescence techniques and by comparison with other geochronometers. For Australian fluvial sediments, comparisons have been made between OSL and TL ages (see “► [Luminescence Dating, History](#)”, for TL); in these instances, the ages commonly overlap within error and have been used to argue for the veracity of TL ages in those settings (Nanson et al. 2005; Maroulis et al. 2007). More commonly, luminescence ages have been compared with chronologies obtained using different techniques on the same sediment layers or from underlying or overlying sediment layers

(e.g., Madsen et al. 2005; Rodnight et al. 2006). For instance, in the Klip River wetlands, South Africa, OSL dating was used to establish the age of sandy paleochannel sediments, while ^{14}C dating (see “► [\$^{14}\text{C}\$ Dating](#)”) was used to establish the age of post-abandonment, organic-rich infills (Rodnight et al. 2006). As expected, the ^{14}C ages tended to be younger than the OSL ages (Fig. 3), thus providing support for the OSL analyses.

Comparison with Other Paleoenvironmental Datasets

Luminescence dating can establish the timing, rates, and nature of sediment movement, but a common aim of geomorphological enquiry is to identify the drivers of change. Drivers of change may be intrinsic to the system dynamics; for example, vertical accretion, lateral migration, and/or forward extension of aeolian dunes, meander bends, or coastal spits (Fig. 2a–c) can occur under conditions of constant sediment supply and steady wind regime, discharge, or wave energy. Commonly, however, drivers of change are extrinsic to the system and result from wider paleoenvironmental changes, including those related to climatic, sea level, tectonic, volcanic, or anthropogenic perturbations. Where paleoenvironmental changes lead to marked increases in the magnitude and frequency of river flooding, for instance, this may lead to increased rates of floodplain vertical accumulation or meander bend migration. These changed rates may be established by OSL dating, but inferences regarding the drivers of change require comparison with independently dated paleoenvironmental datasets. Uranium-thorium-dated (see “► [U-Series Dating](#)”) or ^{14}C -dated lacustrine, cave, or marine deposits, for instance, are commonly used to derive proxy records of paleoclimate change (e.g., past precipitation, temperature, and/or vegetation, or some combination thereof, such as indices of moisture availability). A lack of close correspondence between the timing and rates of landform changes established by luminescence dating and the changes in these proxy records might suggest that the dynamics have been driven independently of paleoclimate, such as by intrinsic system dynamics or by some other paleoenvironmental factor (e.g., past tectonics). Where close correspondence exists, however, this provides a basis for paleoclimatic interpretation of the landform changes, and this line of reasoning has been widely adopted in geomorphological enquiries.

Limitations of Luminescence Dating in Geomorphology

Although the comparison of luminescence chronologies with other paleoenvironmental datasets is common in geomorphological enquiry, potential problems may impinge on this objective. Two common problems are outlined below.

An Inability to Establish Finite Luminescence Ages

Where the sediment being dated has a depositional age that approaches or exceeds the age range of the luminescence technique, then saturation of the luminescence signal may occur (see “► [Luminescence Dating, Uncertainties and Age Range](#)”). In such instances, it may not be possible to determine a finite age, and only a minimum age for deposition can be reported (e.g., >XX years). Although this may provide useful information – for instance, in confirming that basal sediments have minimum ages older than finite ages for overlying sediments – it does not allow calculation of finite vertical accumulation, lateral migration, or forward extension rates and precludes detailed comparison with other paleoenvironmental datasets.

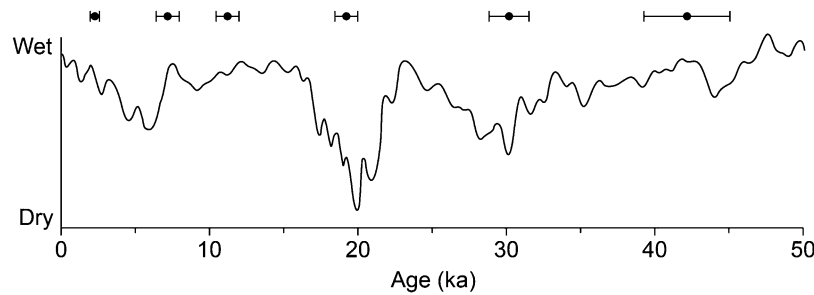


Fig. 4 Hypothetical but realistic illustration of the problems in attempting to correlate luminescence ages (in this instance, from fluvial samples) and associated error bars with the paleoenvironmental changes (paleomoisture index) recorded in higher-resolution datasets for the last 50 kyr. Errors associated with OSL ages generally increase farther back in time and so may encompass one or more peaks and troughs in the paleomoisture index. Consequently, it may not be clear whether periods of fluvial activity identified by the OSL ages have been driven primarily by relatively wet, relatively dry, or transitional (wet-dry, dry-wet) conditions

Limited Precision of Luminescence Ages

Luminescence ages are reported with errors that reflect random and systematic uncertainties; for OSL ages, errors at one sigma (68 % confidence interval) are typically around 5–10 % of the sample age (e.g., see Figs. 2b and 3). Hence, although the central age is the most likely, there is actually a 68 % chance that the sample age lies within the reported error range. In some instances, this means that OSL ages for adjacent landforms will overlap within error, causing uncertainty when calculating rates of change. For instance, across a scroll bar sequence in the Klip River floodplain, South Africa, most OSL ages were in the correct order and did not overlap, thereby indicating an approximately steady lateral migration rate of ~0.16 m/year over the last ~1 kyr. Two ages in the middle of the sequence, however, overlapped within error (Fig. 2b – samples 3 and 4). In such situations, it may be unclear whether the overlapping ages reflect increased analytical uncertainty associated with particular ages or whether they reflect a short-term increase in the lateral migration rate, although the latter explanation was preferred in the Klip River case (see Rodnight et al. 2005). The limited precision of OSL ages also limits the potential for comparison with high-resolution paleoenvironmental datasets derived from, say, lacustrine, cave, or marine sediments; errors on OSL ages may overlap with identified fluctuations in past precipitation, temperature, vegetation, or moisture availability (see Fig. 4), even those occurring over multimillennial scales, such that paleoenvironmental drivers are hard to establish. In the case of alluvial fans in Death Valley, California, USA, Dorn (1996) has argued that imprecision in many geochronometers means that climatic hypotheses of fan formation are not testable; with some caveats, this argument could be extended to OSL analysis of other landforms. Commonly, however, the lack of precision is acknowledged, and correlation with paleoenvironmental datasets is made using the central ages (e.g., Macklin et al. 2010).

Awareness of these limitations is important when considering the applicability of luminescence dating in geomorphological enquiry, and some may be partially overcome by future developments. For instance, ongoing analytical work using thermally transferred OSL (TT-OSL) is attempting to extend the luminescence dating age range (Rhodes 2011); in future, this may enable comparisons with longer paleoenvironmental datasets, possibly including those extending back ~500 kyr or farther, although any finite ages are still likely to be associated with large errors. In other instances, the use of luminescence dating in combination with other geochronometers may provide the best approach. In central Australia, for instance, relatively young luminescence saturation ages (typically <100 ka) mean that OSL cannot be used to determine the age of aeolian linear dunes that may

be many hundreds of thousands or even millions of years old. Hence, Fujioka et al. (2009) combined cosmogenic burial dating (see “► [Cosmogenic Nuclide Dating](#)”) and OSL dating to investigate histories of dune building; cosmogenic (^{10}Be – ^{26}Al) burial dating of the basal sediments helped to determine that the first dunes formed in the western Simpson Desert ~1 Ma, while dating of younger, overlying sediments using OSL indicated that episodic dune reworking and building occurred during late Quaternary glacial intervals. Similarly innovative sampling designs that employ complementary geochronological techniques may be a hallmark of future geomorphological enquiries.

Conclusions

Over the last few decades, luminescence dating has contributed to a revolution in our understanding of the timing, rates and nature of many geomorphological processes, and their implications for landform and landscape development. Despite some limitations, this increased understanding has occurred in parallel with increasing insight into the paleoenvironmental drivers of change. Further innovations in luminescence sampling approaches (e.g., adoption of “range-finder” OSL dating – Durcan et al. 2010) and ongoing analytical advances (e.g., wider application of single grain OSL dating, the increasing use of feldspars as chronometers, and the development of TT-OSL – Rhodes 2011) mean that luminescence dating is likely to remain an essential part of the geomorphologist’s “toolkit” in the decades to come. This will provide fertile ground for interdisciplinary work in scientific and applied contexts, such as in archaeology, paleoanthropology, paleoseismicity, and environmental management (e.g., Rittenour 2008; McCarthy et al. 2010; Barré et al. 2012; see also “► [Luminescence Dating of Archaeological Sediments](#)”, “► [Luminescence, Dispersion of Early Modern Humans](#)”).

Cross-References

- [Cosmogenic Nuclide Dating](#)
- [Luminescence Dating of Archaeological Sediments](#)
- [Luminescence Dating](#)
- [Luminescence Dating, History](#)
- [Luminescence, Deep Sea Marine and Lacustrine](#)
- [Luminescence, Dispersion of Early Modern Humans](#)
- [Luminescence, Earthquake and Tectonic Activity](#)
- [Luminescence, Glacial Sediments](#)
- [Luminescence Dating, Uncertainties and Age Range](#)
- [\$^{14}\text{C}\$ Dating](#)
- [U-Series Dating](#)

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Dendrochronology, Dwellings

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Synonyms

[Tree-ring dating](#)

Definition

Dendrochronology is literally “the study of tree time” and is the science of assigning calendar-year dates to the growth rings of trees. It is based on the fundamental principle of cross dating (Fig. 1), which is classically defined as “the procedure of matching ring width variations. . . among trees that have grown in nearby areas, allowing the identification of the exact year in which each ring formed” (Fritts 1976, p. 534). Cross dating “utilizes the presence and absence of [ring] synchrony from different cores and trees to identify the growth rings that may be misinterpreted” (Fritts and Swetnam 1989, p. 121). Three aspects warrant emphasis. First, tree-ring dating requires ring pattern matching, not ring counting. Second, sample sizes must be large, so that tree-growth variability in a given region is well understood. Third, one begins by studying living trees in a given area, cross dating their ring series internally, and working back in time to successively older specimens that are usually found as dead snags on the landscape or as construction beams in ancient dwellings (Nash 1999).

Methods

The process of dating an archaeological tree-ring specimen requires, first and foremost, creation of a smooth surface on which all the growth rings are clearly visible. This smoothing is achieved using standard wood-working equipment and progressively finer-grit sandpaper (up to American National Standards Institute 400 grit; 20.6–23.6 μm or thousandths of a millimeter), such that individual cell walls on the specimen can be seen. Once a smooth, clear surface is prepared, the dendrochronologist can measure individual ring widths using specialized hardware (like a Velmex™ measuring stage, precise to 0.001 mm, or similar equipment) interfaced with a computer running specialized software (like MeasureJ2X™ software or similar programs). Once all rings have been accurately and precisely measured, open-source COFECHA software is used to compare the ring-width measurement series to previously developed local or regional tree-ring chronologies in order to suggest dating possibilities, which must then be checked against the original wood specimen. If all goes well, calendar dates may then be assigned to each growth ring on that specimen. In places like the American Southwest, where tree growth is often quite sensitive

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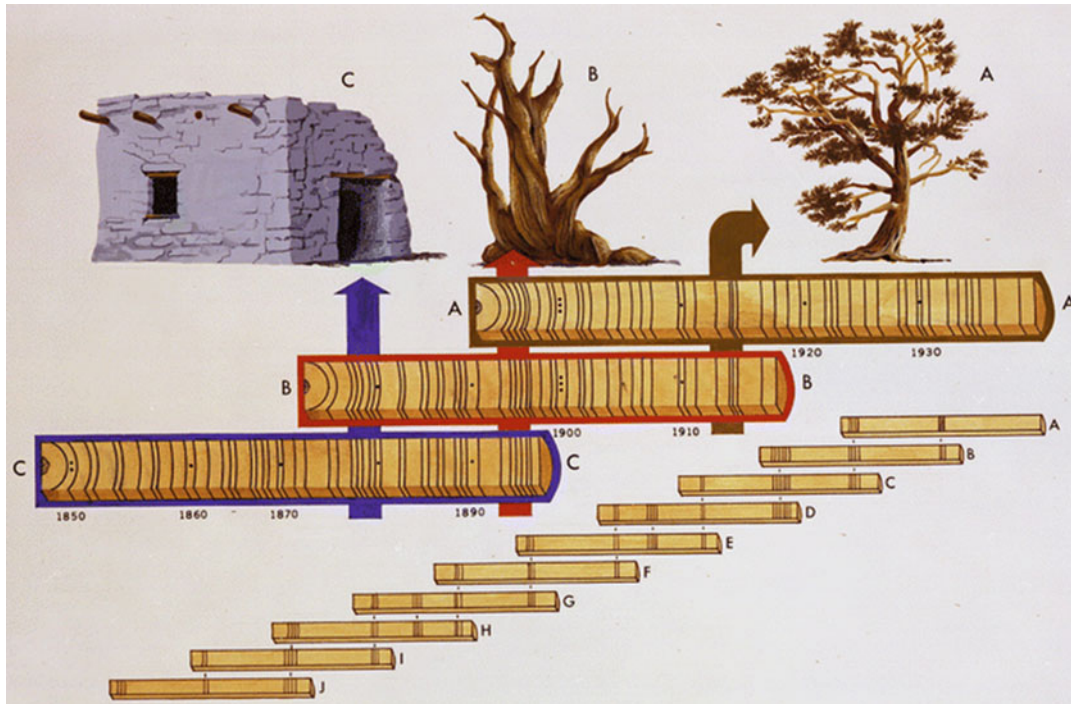


Fig. 1 Cross dating, the basic principle of tree-ring dating, illustrated. The landscape across the American Southwest has living trees, dead but exposed snags and remnant trees, and archaeological wood preserved in existing structures and cliff dwellings. A dendrochronologist begins by analyzing long ring growth patterns in cores from living trees (represented by “A” in the top portion of the figure). He/she then analyzes long ring series in successively older specimens from dead snags and remnant trees (represented by “B” in the top portion of the figure), taking care to make sure that the ring series overlap by at least 50 years. Finally, he/she analyzes ring series in archaeological wood (or charcoal) specimens (represented by “C” above), again making sure that the ring series overlap by at least 50 years, to develop a long master chronology. Once a master tree-ring chronology (represented by A + B + C above; in reality chronologies are based on dozens of specimens) has been developed, newly collected archaeological and historic tree-ring specimens (represented by specimens A through J in the lower portion of the figure) may be analyzed and dated against this master ring-width chronology (Courtesy of the Laboratory of Tree-Ring Research)

to precipitation, cross dating can be performed by hand, as it was originally developed by Andrew Ellicott Douglass in the early 1900s (Douglass 1929; Nash 1999).

In the Douglass method, the dendrochronologist prepares a smooth surface as above but then creates a summary graphic representation of the specimen’s ring-width variability known as a skeleton plot, in which long lines are written on graph paper to indicate relatively narrow rings, a “B” indicates a relatively large ring, and in which other unique attributes (e.g., wide or narrow earlywood or latewood bands) are noted that may assist in dating (Fig. 2; see Stokes and Smiley 1968). The skeleton plot is then visually compared to the previously developed local or regional master tree-growth chronology. When the ring-width pattern summarized on the skeleton plot matches the local or regional growth pattern on the master chronology and all missing, double, or locally absent rings on the specimen have been identified, an accurate and precise date can be assigned to all rings on that specimen.

From a dendrochronological perspective, all cross-dated and verified tree-ring dates are created equal; there is no statistical uncertainty associated with cross-dated tree-ring dates, which are the most precise chronometric data available to archaeologists in the absence of historic records (Jacoby 2000). Unfortunately, and for a variety of reasons including chaotic or complacent ring growth, poor preservation, and other factors, many tree-ring specimens simply cannot be dated,

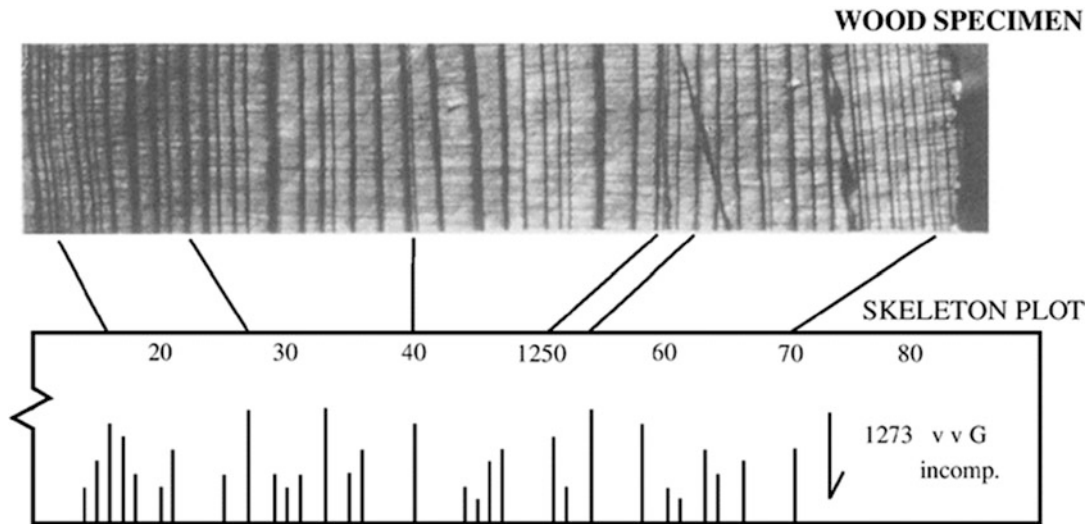


Fig. 2 A skeleton plot for a wood specimen collected from a cliff dwelling in the American Southwest. Especially long lines on the graph represent especially narrow rings on the specimen, which are caused by especially dry years in the tree's existence. The date for the last ring present on the specimen is A.D. 1273; the "vv G incom." suffix describes noteworthy specimen attributes that modify the outside date. The "vv" indicates that it is a noncutting date and that there is no way of estimating how far it is from an actual date-of-death of the tree. The "G" indicates, however, that galleries from wood-boring beetles are present on the outside of the specimen; the "incomp." indicates that the outer growth ring is incomplete, suggesting that the tree was cut down during its growth season, usually late spring or early summer (Courtesy of the Laboratory of Tree-Ring Research)

either quantitatively or by the Douglass method. In this situation, dendrochronologists should not succumb when archaeologists ask for a "likely date" for a specimen, nor should they use independent archaeological data to propose a probable date for an undated specimen (Baillie 1995). Once a cross-dated tree-ring date is determined, the interpretation of that date within its archaeological context becomes the archaeologist's responsibility (Dean 1978). From this perspective, all tree-ring dates are *not* created equal, and an extensive body of theory has been developed to guide the proper interpretation of archaeological tree-ring dates (Bannister 1962; Dean 1978; Hillam 1987, 1998).

Tree-ring dating is most commonly used in the North American Southwest, where ponderosa pine (*Pinus ponderosa*), Douglas fir (*Pseudotsuga menziesii*), pinyon pine (*Pinus edulis*), and juniper (*Juniperus scopulorum*) are sensitive to variations in precipitation, are well preserved in the archaeological record, and were commonly used by indigenous populations. Dated sites include cliff dwellings like those at Mesa Verde National Park, standing architecture at Chaco Canyon National Historical Park, and pit houses across much of the region. In the southeastern United States, researchers focus on dating baldcypress (*Taxodium distichum*), juniper (*Juniperus sp.*), white oak (*Quercus alba*), and other species. Dated sites include standing historic structures and a very small number of archaeological sites, which remain poorly dated because wood specimens are not well preserved in wet environments and because historic deforestation in the region makes it difficult to build long chronologies going back in time. In Western Europe and the Mediterranean, dating efforts focus on oak (*Quercus sp.*), juniper (*Juniperus sp.*), and other species, which are used to date churches, dwellings, ship wrecks, and a wide variety of other archaeological and historic features (Nash 2002).

In theory, tree-ring dating is a relatively straightforward process; in practice it can be astonishingly difficult. It requires rigorous sample collection and preparation, methodical attention to

detail, and deep knowledge of tree-growth characteristics and wood attributes across vast regions. For additional information and resources on the method, theory, and results of tree-ring dating, see Henri Grissino-Mayer's excellent *Science of Tree-Rings* website (<http://web.utk.edu/~grissino/>; accessed 14 August 2013).

Origins

Andrew Ellicott Douglass, the father of dendrochronology, introduced tree-ring dating in “Talkative Tree-Rings and the Tales They Tell,” published in the December, 1929, issue of *National Geographic* magazine (Douglass 1929). He offered tree-ring dates for dozens of archaeological sites in the American Southwest. As a result, archaeologists were forced to revise their interpretation of southwestern prehistory, for they had grossly overestimated the age of the ruins (Nash 1999). Nearly as important, however, was Douglass' inference that a “Great Drought” had occurred across the American Southwest from A.D. 1276 until 1299 and that it had affected pre-Columbian populations living in the area, thus, also began the field of dendroclimatology.

Types of Information

The analytic and interpretive utility of tree-ring dating stems from the fact that it can inform archaeological research in three broad arenas: chronometric, environmental, and behavioral (Dean 1996a). The chronometric aspect of tree-ring dating has the longest history and is the most commonly known – tree rings can be used to date objects, features, dwellings, and sites. By extension, tree-ring dates can be used to date abstract archaeological entities such as periods, stages, phases, and styles. The environmental aspect of modern tree-ring dating today enjoys the most worldwide application, as tree rings can be used to reconstruct numerous environmental variables, including temperature, precipitation, stream flow, drought severity, fire frequency and intensity, insect infestation, atmospheric circulation patterns, and others. The behavioral aspect of tree-ring dating allows archaeologists to make inferences regarding wood-use practices, trade, and other economic variables (Dean 1996b; Towner and Clary 2001; Towner et al. 2009; Towner and Creaseman 2010; Windes 2010).

Cutting Dates, Noncutting Dates, and Date Clusters

The difference between cutting dates and noncutting dates is important, as is the concept of date clustering. *Cutting* dates are assigned to cross-dated wood or charcoal specimens that possess evidence that the last ring present on the specimen was the last ring grown by the tree before it died. *Noncutting* dates are assigned to cross-dated specimens if there is no evidence indicating that the last ring present on the specimen is the last one grown before the tree died. Note that cutting and noncutting dates are not mutually exclusive – a noncutting date *may* actually record the date of a tree's death, but there happens to be no discernable, definitive criteria (e.g., bark, beetle galleries, patinated surfaces) present on the specimen that allow the “cutting date” designation. Noncutting dates are therefore potentially biased estimates of beam procurement and use events because they underestimate the actual date-of-death of the tree (Ahlstrom 1997).

The archaeological interpretation of noncutting dates is complicated because there is no way of knowing, a priori, how many rings are missing from the outside portion of the specimen. The vagaries of tree growth, site formation processes, specimen preservation, and wood-use behavior ensure that only a fraction of tree-ring specimens submitted for analysis date and, of those that do, most yield noncutting dates because the outer portion of a beam is more likely to be lost due to decay, insect infestation, or anthropogenic removal. Despite recent efforts to alleviate the interpretive difficulties associated with noncutting dates, they remain the most recalcitrant of tree-ring dates for archaeological purposes (Nash 1997).

Another concept useful for the interpretation of tree-ring dates is *date clustering* (Ahlstrom 1985; Baillie 1995). If a number of tree-ring dates from a given site or provenience cluster in one to three calendar years, one can infer that some construction event occurred and has been dated by the tree rings. For the archaeologist interested in determining an accurate and precise date of construction for a given room or site, the ideal date distribution curve would consist of a vertical line of x number of cutting dates in a given year. Because of activities such as beam stockpiling, manipulation, reuse, and structure repair, actual date distribution curves are often skewed left, with long tails, as noncutting dates dominate the distribution (Ahlstrom 1997, p. 343; Ahlstrom and Smiley 1998, p. 150).

Cutting Date Estimation

Dendrochronologists have attempted to estimate cutting dates for specimens that yield only noncutting dates, the logic being that if the number of missing rings can be estimated with some reasonable degree of probability, one can then simply add the estimated number of rings to the existing outer ring date to obtain an estimated cutting date. In general, there are three techniques for estimating cutting dates (Hughes et al. 1981). The first is to determine some statistical relationship between the number of sapwood rings, and therefore the number of rings that might be lost, and various tree-growth parameters. The second is merely to assume an immutable number of sapwood rings. The third is to calculate the mean and standard deviations of the number of sapwood rings from frequency distributions of samples assumed to be from the same statistical populations.

Nash (1997) used heartwood and sapwood data from living-tree cores to calculate regression equations that predict the number of sapwood rings on a specimen based on the number of heartwood rings. Using case studies from the well-dated protohistoric, historic, and modern dwellings at Walpi, Arizona, he concluded that because of the statistical uncertainty associated with estimated cutting dates, they are best considered in the aggregate, in terms of the site's entire date distribution curve.

Cutting-dating estimation is much more common in Europe than in North America. Empirical research has now been extensive enough to document a decreasing west–east gradient in the number of sapwood rings found in European oaks: In Ireland, mature oaks tend to have 32 ± 9 sapwood rings; German oaks tend to have 19 ± 8 sapwood rings, while Finnish oaks have 14 ± 3 (Baillie et al. 1985; see Pilcher 1987).

Recent Research

Nash (2002) and Towner (2002) published their perspectives on the status of American archaeological tree-ring dating at the turn of the millennium; Baillie (2002) and Kuniholm (2002) did so for

Europe and the Mediterranean, respectively. Since then, the bulk of published research on the dendrochronology of ancient dwellings has occurred in the southern and eastern United States, in Western Europe, and, to a lesser degree, in the greater Mediterranean area. In a stunning recent development, the full implications of which will take years to realize, Morales et al. (2013) dated pre-Hispanic *chullpas* (burial towers and storage chambers) in the Andean Altiplano, marking the first time that reliable tree-ring dates have been obtained for archaeological structures in South America.

Grissino-Mayer (2009; see also references therein) and colleagues led the effort to date historic structures in the eastern and southern United States, publishing a special issue of the journal *Tree-Ring Research* in the process. The effort to use tree rings to date historic structures often begins with a disagreement about the purported age of the structures, which often stems from a lack of concordance between documentary evidence and oral histories. Dendrochronological specialists are then called in to provide a complementary dataset. Much to the chagrin of local heritage specialists, however, tree-ring dates can undermine previously held ownership histories for individual structures. How, for example, can the John Sevier Cabin have been occupied by Tennessee Governor Sevier, who died in 1815, if tree-ring dates indicate that the cabin was built sometime between the summer of 1835 and the early spring of 1836 (Slayton et al. 2009, p. 35; for additional examples see also Grissino-Mayer and van de Gevel 2007; Towner 2008)?

In other instances, tree-ring dates confirm, or at the least do not contradict, previously held interpretations about settlement origins and histories, including a slave cabin at The Hermitage, President Andrew Jackson's estate (Lewis et al. 2009), an antebellum plantation house in Arkansas (Therrell and Stahle 2012), an antebellum house in Georgia (Wight and Grissino-Mayer 2004), and structures in southeastern Nova Scotia (Robichaud and Laroque 2008), among many others.

In Western Europe (and also in the American Southwest), much archaeological tree-ring dating is driven by heritage resource management; tree-ring dates and interpretive results are therefore often published in proprietary reports. English Heritage has, however, made available more than 100 tree-ring dating reports (search "tree-ring dating" and "dendrochronological analysis" at <http://research.english-heritage.org.uk/>; accessed 21 May 2013) on dwellings, churches, and other structures throughout the United Kingdom. Hoffsummer (2009; see also Lambert 2009; Trenard 2009; Haneca and Debonne 2012) discussed the issues complicating tree-ring dating of European structures in an edited volume on the typology and development of roof frames in Belgium and northern France from the eleventh to the nineteenth centuries. Tegel et al. (2012) used tree rings to date early Neolithic water wells, which they describe as the earliest wood architecture but is more accurately described as the earliest *tree-ring-dated* wood architecture. Further to the east, Bernabei and Bontadi (2012) used tree-ring dating to identify previously undocumented, or poorly documented, construction activity at the Church of the Nativity in Bethlehem. They dated previously undocumented repair events between A.D. 1000 and the early 1200s and conclusively identified the source of wood, far afield in the Republic of Venice, for a massive mid-fifteenth-century repair event. The Aegean Dendrochronology Project, formerly based at Cornell University, has moved to the Laboratory of Tree-Ring Research at the University of Arizona in Tucson, where it continues a long tradition of dating ancient dwellings in the greater Mediterranean region.

Summary

Nearly a century after Douglass (1929) demonstrated that tree rings could be used to date ancient dwellings, the interpretation of archaeological tree-ring dates has become more sophisticated with

respect to understanding prehistoric wood-use behavior and the discrepancies that sometimes occur between historic documentation, oral history, and tree-ring data. Arguably even more impressive, however, is the fact that tree-ring dating is now routinely applied in areas like eastern and southern North America, in which scholars once believed tree-ring dating would not be successful. The expansion of tree-ring dating to South America and the tropics has the potential to be revolutionary, if sites with well-preserved wood can be found in quantity.

Cross-References

- ▶ [14C Dating](#)
- ▶ [Dendrochronology, Palaeoclimate](#)
- ▶ [Dendrochronology, Progress](#)
- ▶ [Geochronology](#)
- ▶ [Historical Development \(of Dating Methods\)](#)

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Luminescence, Volcanic Rocks

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Definition

Luminescence dating methods are applicable to estimate ages of past volcanic eruptions using (1) volcanic phenocrysts (quartz and feldspar) and glass within volcanic rocks (including unconsolidated tephra) and (2) rocks heated by lava or pyroclastic flow. Unlike luminescence dating of light-exposed sediments, the luminescence clock is reset by heating or is naturally zero at the time of crystallization. Another resetting mechanism of temperature-assisted hydrostatic pressure by phreatic eruptions has been also proposed (Zöller et al. 2009).

Introduction

The first attempt of luminescence dating of volcanic rocks has been done by Wintle (1973) using thermoluminescence (TL) of rhyolites and basalts containing plagioclase phenocrysts. She found, however, a significant signal loss in artificially irradiated samples after a storage, which is known as anomalous fading, leading to an age underestimation. Since then, luminescence dating studies using quartz, feldspar, and volcanic glass have been done both using TL and optically stimulated luminescence (OSL). A comprehensive review of luminescence dating of volcanic products was published by Fattahi and Stokes (2003).

Quartz

Dating applications using quartz is possible for both quartz-bearing tephra having rhyolitic composition and rocks heated by lava or pyroclastic flows. Quartz-bearing tephras were dated initially by TL in the blue detection wavelength (e.g., Ichikawa et al. 1982; Takamiya and Nishimura 1986). Later, Hashimoto et al. (1986) found that volcanic quartz has a TL peak in the orange-red region (~ 620 nm) at around 380°C . This peak has a higher saturation dose than that of the blue TL peak at ~ 470 nm (Hashimoto et al. 1987; Miallier et al. 1991). Since then, red TL has been used to date volcanic quartz successfully both using multiple-aliquot (e.g., Miallier et al. 1994; Pilleyre et al. 1992) and single-aliquot (e.g., Toyoda et al. 2006) approaches. The high saturation dose (characteristic saturation dose, $D_0 \sim 6,500$ Gy) made it possible to date a tephra older than 1 Ma (Fattahi and Stokes 2000). However, the measurement of red TL needs a PM tube which is more sensitive to longer wavelength (trialkali or GaAs tubes), and the tube has to be cooled to reduce dark counts. A high blackbody radiation is also expected. In order to subtract the blackbody radiation more easily from the red TL signal, the use of isothermal TL, by keeping

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temperature the same for a prolonged time, has been proposed (Tsukamoto et al. 2007; Ganzawa and Maeda 2009). Dating of tephra using red TL has been also done using quartz single grains from tephra (Ganzawa and Ike 2011). OSL using single-aliquot regenerative dose (SAR) protocol has been tested for dating volcanic rocks (Bonde et al. 2001). However, OSL of volcanic quartz has been found to fade and has lower thermal stability than sedimentary quartz (Tsukamoto et al. 2007). But these problems do not exist in the case of quartz which originated from nonvolcanic bedrocks. OSL dating was successfully applied for samples from Eifel volcanic field, Germany, where high-pressure shock waves during phreatic eruptions had probably reset the OSL signals (Preusser et al. 2011).

Feldspar

After the finding of anomalous fading by Wintle (1973), there have not been many studies on luminescence dating of volcanic feldspars until very recently, because of the difficulty in dealing with high fading rates. May (1977) investigated TL of plagioclase feldspars from alkali and tholeiitic basalts with known ages from Hawaii and found a correlation between normalized natural signal intensities and expected ages up to 200 ka, despite the presence of significant anomalous fading. Guérin and Valladas (1980) studied TL in the UV detection wavelength at high temperature ($>580^{\circ}\text{C}$) from volcanic plagioclase from France and concluded that the high-temperature TL peak is not significantly affected by anomalous fading. TL from sanidine in the far-red region ($\sim 710\text{ nm}$) was also found to be not affected by anomalous fading (Zink et al. 1995; Visocekas and Zink 1999). Recently, the possibility of luminescence dating on the Martian surface has been suggested (McKeever et al. 2003), and since then a growing number of studies have been published (e.g., Kalchgruber et al. 2006; Jain et al. 2006). Morthekai et al. (2008) and Tsukamoto and Duller (2008) compared fading rates of various luminescence signals from Martian analog materials on Earth. While Morthekai et al. (2008) obtained the lowest fading rate from red TL (630–670 nm) signal from andesite and basalt samples, Tsukamoto and Duller (2008) reported relatively uniform fading rates of 5–7 %/decade from IRSL signal at 200°C from basalts in the blue detection wavelength. Following this, Tsukamoto et al. (2010, 2011) dated andesitic tephra and basalts using IRSL at 200°C and obtained consistent ages with independent age controls up to $\sim 70\text{ ka}$. Scoria samples from Vesuvius containing leucite and sanidine have been dated using post-IR IRSL method (Tsukamoto et al. 2014), which has been developed to minimize anomalous fading (Thomsen et al. 2008). The fading rate was successfully reduced from $\sim 30\%$ to less than 5% by increasing both preheat and post-IR stimulation temperatures, and the ages after fading correction agreed with known eruption ages of Vesuvius (Tsukamoto et al. 2014).

Volcanic Glass

TL dating of volcanic glass has been first reported by Berger and Huntley (1983) using 2–11 μm fraction of glass. Fine grain volcanic glass was selected, because it was homogeneous and it was certain that it originated primarily from the eruption (without lithic fragments). This work was followed by Berger (1985, 1992) who dated volcanic ashes between 8 and 400 ka using TL in blue-green detection wavelength using multiple-aliquot additive dose technique. TL spectra were measured from volcanic glass from tephra in Japan by Kanemaki et al. (1991). They found that the TL spectra from volcanic glass are similar to those of quartz and plagioclase phenocrysts, and

therefore, the TL from volcanic glass originates from quartz and/or plagioclase microcrystals in the glass. Optical dating of volcanic glass has been tested by Berger and Huntley (1994). The OSL and IRSL signals from volcanic glass from 15 samples are generally dim, and they concluded that the optical dating of volcanic glass is only occasionally feasible. However, Biswas et al. (2013) used fine grain volcanic ashes (4–11 μm) which are presumably dominated by volcanic glass and applied post-IR IRSL protocol. The intensity of post-IR IRSL signal was much larger than IRSL at 50 °C and it showed negligible anomalous fading.

Summary

Red TL dating using volcanic quartz has been proven to be a powerful dating technique to date rhyolitic tephra. Different measurement methods (red TL, UV-TL, and IRSL) have been suggested to be useful in dating volcanic feldspars. Since the post-IR IRSL technique has been successfully applied in dating sedimentary feldspar without a fading correction, this method should be tested more for volcanic feldspars. Volcanic glass has a problem of low luminescence sensitivity, but the post-IR IRSL is helpful in both reducing anomalous fading and increasing luminescence intensity.

Cross-References

- [Luminescence Dating](#)
- [Luminescence, Martian Sediments](#)

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Radiocarbon Dating

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Synonyms

¹⁴C dating; Carbon dating; Carbon-14 dating; Radiocarbon dating

Definition

Radiocarbon dating is a method of measuring the age of organic or carbonate phases in radiocarbon years by the level of the nuclide ¹⁴C remaining in the sample. Calibration of the radiocarbon age is done by comparison to known-age records such as tree rings. Stuiver and Polach (1977) define a radiocarbon date to include five things: (a) the use of the 5,568-year half-life (mean life 8,033 years); (b) the assumption of constancy of ¹⁴C atmospheric level during the past; (c) direct or indirect comparison to a known standard, oxalic acid; (d) isotopic fractionation normalization of all sample activities to the base of $\delta^{13}\text{C} = -25\text{‰}$; and (e) the year 1950 which is automatically the base year, with ages given in years BP (i.e., where present is defined as AD 1950).

Introduction

Radiocarbon (carbon-14 or ¹⁴C) is produced in the upper atmosphere by the action of cosmic ray-induced radiation on nitrogen in the atmosphere. The nuclear reaction ¹⁴N(n, p)¹⁴C has a high cross section of 2.5 barns. The production rate of ¹⁴C is estimated to average ~2.2 atoms/cm²/s (Usoskin and Kromer 2005). Once produced, ¹⁴C is rapidly incorporated into the atmosphere as CO and then oxidized to CO₂. In this form it makes its way into the terrestrial biosphere through photosynthesis, through the carbon cycle. The time scale of this process is rapid, so that ¹⁴C in the atmosphere and the biosphere are in equilibrium on a time scale of <1 year (see Fig. 1). Radiocarbon dating is one of the most important isotopic geochronological methods and has an immense range of applications to scientific studies including archaeology, geology, and oceanography. The development of radiocarbon dating changed the way that geologists and archaeologists look at chronology (Renfrew 1979).

The radioactive decay equation gives the relationship between the decay rate and the number of ¹⁴C atoms that will decay with time according to the radioactive decay equation (Rutherford and Soddy 1902):

$$dn/dt = -\lambda N \quad (1)$$

In this equation the decay rate (dn/dt) is directly proportional to the number of radioactive atoms

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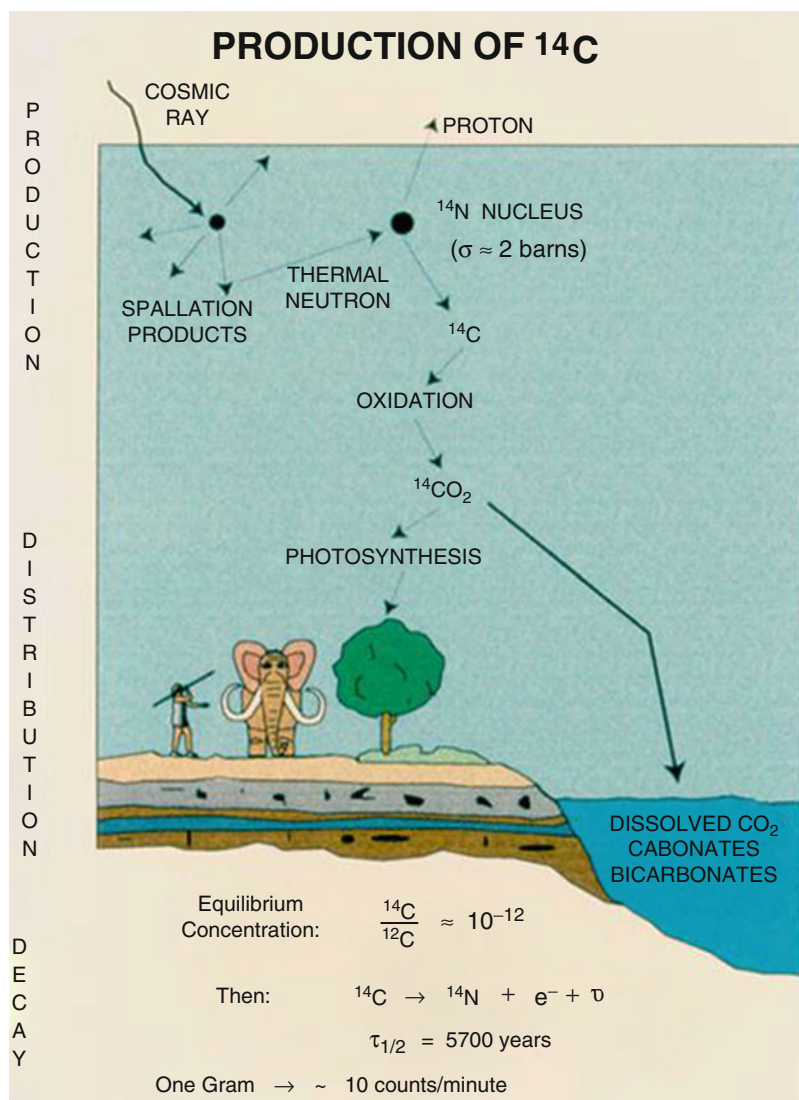


Fig. 1 A diagram of radiocarbon dating

present (N). The “decay constant” λ defines the rate of decay. The decay constant is related to the “half-life” $t_{1/2}$ of a radionuclide as the time required for $\frac{1}{2}$ of the remaining atoms to decay. The half-life is related to the decay constant by the relation:

$$t_{1/2} = \frac{\ln 2}{\lambda} \quad (2)$$

By convention, a radiocarbon date implies a half-life of 5,568 years, as originally proposed by Willard Libby (1955). The useful limit of the technique is around 50,000 years in a typical radiocarbon laboratory. This explains the great facility of the method which can be used, for example, to date the most recent global glacial-interglacial advances and retreats, the development of modern humans, and the rise of civilizations. Hence, it covers a time scale of fundamental importance to geology and archaeology. It should be noted that Libby’s half-life determination has since been revised to 5,730 years, but radiocarbon dates are still calculated with the 5,568-year value by convention. This allows for unambiguous comparisons between radiocarbon dates, regardless of

when the measurements were made. This difference introduces a 2 % offset which is compensated for when the dates are calibrated to calendar years (see below).

We can integrate Eq. 1 with appropriate limits to obtain the equation:

$$\frac{N}{N_0} = e^{-\lambda t} \quad (3)$$

Where N_0 is the number of atoms at time $t = 0$ and N is the number of atoms at any time t . This is the common expression of how the remaining amount of carbon-14 relates to time. It is equally valid to use the activity (or the decay rate), since from Eq. 1, these would obey the same equation.

Originally, radiocarbon measurements were performed by counting the radioactive decay of the ^{14}C isotope (Cook and van der Plicht 2007). We can count either the decays of the ^{14}C , because it emits a β -particle, or we can count the atoms themselves. In recent decades, the method of *accelerator mass spectrometry* (AMS) has gradually taken over the measurement of radiocarbon, and now, most measurements are made by AMS (Burr and Jull 2009). The older counter methodology is still used and can be applied to counting of both liquid samples and gas, especially when sufficient material is available (Longin 1971; Cook and van der Plicht 2007).

If we look at Eq. 1, it should be clear that it is more effective to measure atoms than decays: for modern ^{14}C , the decay rate (A_0) is 13.59 decays per minute per gram of C. In AMS, we typically measure a sample of 0.5 mg C, and we can count over 120,000 atoms from a modern sample. If we take a counting rate of 120,000 atoms in 1,080 s, or 111 counts/s – from 0.5 mg of carbon – then this translates to $111 \times 60/0.0005 = 1.33 \times 10^7$ counts per minute per gram.

A basic assumption of radiocarbon dating is that we know the ^{14}C age of the starting material at the time when the sample was formed. This makes it possible to solve the radioactive decay equation (3), which can be expressed as a ratio of the number of atoms, the isotopic ratio relative to a stable isotope, or the activity (decay rate) ratio. We can define the “fraction of modern carbon,” F :

$$F_{(-25)} = \frac{{}^{14}\text{C}/{}^{13}\text{C}_{S[-25]}}{{}^{14}\text{C}/{}^{13}\text{C}_{1950[-25]}} \quad (4)$$

where the subscript $S [-25]$ refers to the sample renormalized to a $\delta^{13}\text{C}$ value of -25‰ and 1950 refers to the standards discussed above, renormalized to 1950 AD, and $\delta^{13}\text{C} = -19\text{‰}$ for OXI and -25‰ for OXII, or other secondary standards referenced to the oxalic acid standard (Stuiver and Polach 1977). An equivalent expression could be written using atomic ratios (N/N_0) or activity ratios (decay rate, A/A_0) for the sample and standard instead of the isotope ratio $^{14}\text{C}/^{13}\text{C}$, in which case N_0 is the number of atoms at time zero, N is the number of atoms remaining, t is the time in years, and λ is the decay constant. We could also substitute the isotopic ratio $^{14}\text{C}/^{12}\text{C}$, also equivalent to activity (A), referenced to a zero-aged value, $^{14}\text{C}/^{12}\text{C}_0$, or A_0 . All these values would be normalized to $\delta^{13}\text{C}$ at -25‰ . As noted above, the decay constant λ used here assumes a half-life of 5,568 years.

To calculate an age, the decay of ^{14}C is written in terms of F as follows:

$$F_{(-25)} = e^{-\lambda t} \quad (5)$$

and rearranging this equation gives an expression for calculating the *uncalibrated radiocarbon age* of a sample:

$$\text{age} = -8033 \ln F_{(-25)} \quad (6)$$

This age is an uncalibrated result, since it assumes that radiocarbon decays from a constant value. This is usually called the “radiocarbon age.” We know that, due to fluctuations in atmospheric production of ^{14}C , we need to correct for the difference from the “zero” age value. In order to do this, we need a suite of materials of known age and their corresponding apparent “radiocarbon ages.” This process is called “calibration” and is an important step for precision dating using carbon-14.

Calibration

One of the potential problems of radiocarbon dating is that it is assumed that the activity (A_0) or number of atoms (N_0) at the time of production of the sample is always the same. This is not the case. We know that ^{14}C in known-age tree rings fluctuates with time due to several factors, including the level of CO_2 in the atmosphere and cosmic-ray fluctuations due to changes in the Earth’s magnetic field and other effects (Burr 2007). To correct for these problems, an international calibration team has made a cross-calibration of ^{14}C against other records – predominantly *dendrochronology*, *U–Th dating* of corals, *U–Th-dated speleothems*, and *varved-sediment* records. These calibrations are published and revised every 4–5 years. The most recent one is INTCAL13 (Reimer et al. 2013), which refines the curves presented previously derived by INTCAL09 (see Fig. 2).

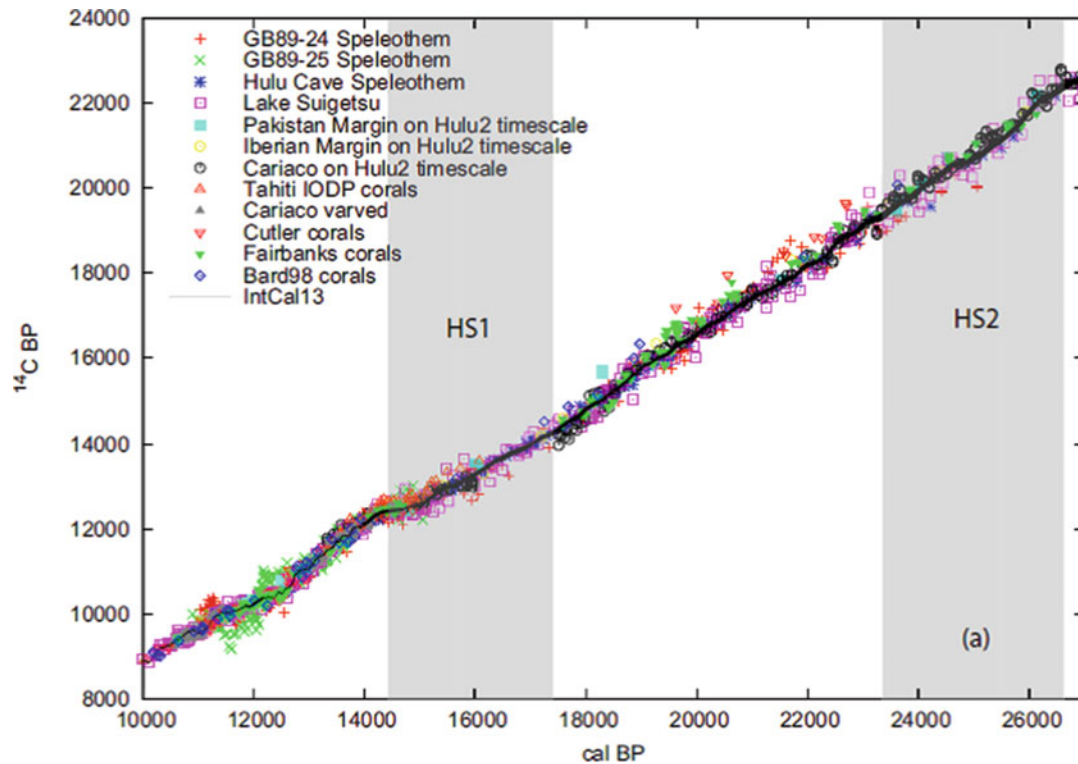


Fig. 2 The calibration curve for the period 10,000–26,000 years (Reimer et al. 2013). The horizontal axis shows the true age based on various records, and the vertical axis displays the radiocarbon age

Fossil-Fuel and Bomb Carbon-14

Another complication is that fossil fuel burning added ^{14}C -free carbon dioxide to the atmosphere resulting in decreased levels of ^{14}C from about 1780 to 1950 AD. Since 1950 AD, we have experienced an increase due to the addition of high levels of ^{14}C from atmospheric nuclear weapons testing. Although most testing was banned after 1963, this is an important signal added to the atmosphere in the last 60 years. The bomb-carbon record is well established and can be used to pinpoint specific dates in the time period since 1950 AD (Burr 2013). Indeed, this signal increases to a maximum of almost twice the pre-bomb level and has since decreased. Various plots of the bomb-curve profile are shown in the bomb-carbon section of this encyclopedia. It is very useful in applications where we need to resolve if a material was produced in the last 60 years – for example, in determining forgeries in the artwork or in forensic applications.

Using Radiocarbon Dating

We can use radiocarbon dating to estimate the age of a wide variety of carbon-containing materials. Both organic and inorganic materials at the Earth's surface and in the oceans form in equilibrium or in steady-state conditions with the atmospheric ^{14}C . This allows us to determine the initial level of ^{14}C and their ages. When an animal or plant dies, the level of ^{14}C decays according to Eq. 3. There are a vast number of applications of ^{14}C , and more details of ^{14}C dating are given in other sections of this encyclopedia.

Sample Preparation

Before measurement of ^{14}C , it is important to clean the sample, so that any ^{14}C that we measure comes from the sample itself and not from contaminants introduced from surrounding environment where the material was found. After we clean the material, we need to convert it to a form suitable to the measurement technique employed: this could be CO_2 gas or benzene for liquid-scintillation counting or solid graphite or CO_2 gas for AMS.

Pretreatment Protocols

The most basic of all pretreatments is the acid-base-acid (ABA) or acid-alkali-acid (AAA) cleaning method for treating a wide range of organic materials, which can include *charcoal*, *wood*, *cellulose*, *plant material*, and *animal remains*. After a physical inspection, samples are cleaned with the addition of a sequence of steps, including (1) HCl acid with a sufficient concentration to dissolve carbonates, usually 1 N HCl, (2) 0.1 % NaOH, and (3) HCl acid. Following each step, the samples are neutralized with distilled water. Following the last step, they are dried. The dried sample is then combusted at 900–1,100 °C with CuO or oxygen gas. There are many refinements of this method. For example, Hatté et al. (2001) identified potential contamination in the ABA pretreatment which can affect wood and paleosol dates and suggested improvements to avoid them. Although charcoals are generally excellent material for dating, Bird et al. (1999) recommended the use of a more severe oxidation step using chromic acid for purification of some old charcoals (Bird et al. 1999). Rebollo et al. (2008) looked at the chemical and structural changes in charcoals pretreated with the ABA

method, and they suggested several modifications to the ABA method based on their findings, including the use of weaker acids, eliminating the initial acid step, treatment with distilled water, and agitation in the alkali step. In another case, Ascough et al. (2011) reported that for some charcoals the alkali-soluble fraction normally removed from the charcoals may be degradation products of the charcoal itself, so removing them does not necessarily improve the cleanliness of the sample.

Other types of samples need other specialized treatment. Carbonate samples are etched using 100 % H_3PO_4 to remove 50–85 % of the carbonate, then dried and acidified with H_3PO_4 , and the carbon is collected as CO_2 . Sediments are treated in a number of ways. One approach is to use selective combustion. After cleaning and drying the sample, the sample is combusted stepwise, at successively higher temperatures to liberate different organic components according to their combustion temperatures (McGeehin et al. 2001).

Radiocarbon dating of works of art and other artifacts is an important application. Usually, textiles, parchment, canvas, and artworks (e.g., canvas from a painting) are cleaned in a Soxhlet apparatus, which utilizes hot solvents to remove contaminants. Typically, a series of solvents such as hexane, ethanol, methanol, and acetone are used (Jull et al. 2004; Hajdas 2008, 2009; Brock 2013). The samples can then be cleaned with distilled water and dried, before combustion at up to 1,100 °C. Iron artifacts can be dated either by melting the sample in an oxygen atmosphere and extracting CO_2 or by using wet-chemical techniques (Park et al. 2010).

There are some excellent examples that illustrate the use of radiocarbon dating for artworks. The most famous is the Shroud of Turin (Damon et al. 1989), but the list also includes the Dead Sea Scrolls and a more recent example is the Voynich manuscript (Zyats et al. 2012) and the *Egyptian Book of the Dead* (Fig. 3).

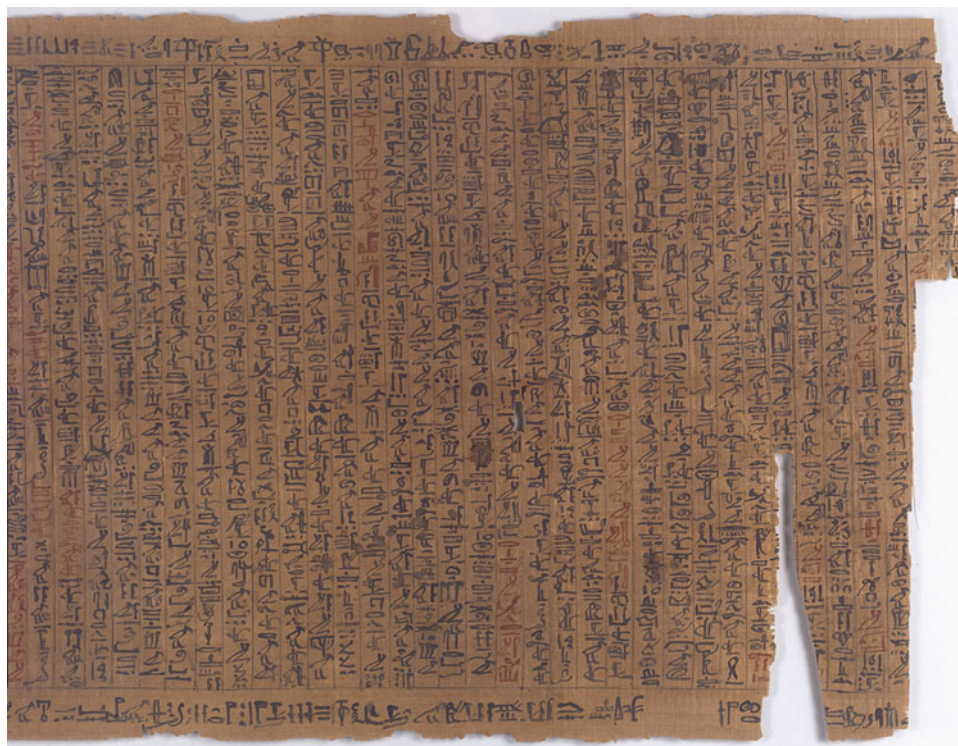


Fig. 3 An example of radiocarbon dating – Egyptian Book of the Dead. This document dates to 1620–1430 BC based on the calibrated age, or $3,249 \pm 49$ radiocarbon years before present (Image courtesy Brooklyn Museum of Art)

There are many specialized approaches to dating bones. Much attention is given to bone pretreatment because of their critical role in archaeological studies and the complexities of bone chemistry. The standard pretreatment method for bone is the collagen extraction technique of Longin (1971). Collagen is a fibrous protein and the principal constituent of bone. This material degrades with time as a result of postdepositional alteration and eventually breaks down into individual amino acids. Bone collagen may interact with exogenous organics through reactions in the burial environment. As a result, a number of screening procedures have been developed to characterize the degree of preservation for individual samples (van Klinken 1999). The most common screening procedure for AMS is the determination of percent collagen in a sample, usually by measuring the elemental C/N ratio. Modern bone consists of ~22 wt% collagen, and this value decreases with burial age. Samples with as low as 0.5 % collagen may be datable, but often require specialized chemical pretreatment, such as the isolation and analysis of individual amino acids (Van Klinken 1999). Samples with <0.5 % collagen are generally considered unsuitable for obtaining a useful date. Another refinement of the collagen extraction technique has become standard in the past decade, using ultrafiltration to isolate the >30 kD molecular weight fraction. The method is highly selective and has been shown to remove contaminants better than the standard collagen extraction technique (Brown et al. 1988). Brock (2013) has also applied the collagen approach to parchment dating.

Groundwater and surface waters can be dated by extracting dissolved inorganic carbon by acidification, in the same manner as solid carbonates are processed. Additionally dissolved organic carbon can be extracted using either KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ as an oxidizing agent (Leonard et al. 2013). We can use these values of ^{14}C to better understand the circulation of groundwater and carbon cycling in lakes (e.g., Yu et al. 2007) and determine reservoir ages.

These are just a few examples of pretreatment methods for typical samples. Specialized techniques that are beyond the scope of this discussion have been developed to pretreat a wide range of samples (see, e.g., Hajdas 2009). The goal of the pretreatment in these cases is to isolate a carbon fraction that was in equilibrium with the atmosphere when it formed and has not been contaminated. For AMS, once the carbon has been extracted, it can be converted to graphite (a common target material in AMS machines) by means of a catalytic decomposition reaction, using Fe as the catalyst. For liquid-scintillation spectrometry, the CO_2 must be converted to benzene, which involves several additional chemistry steps (Cook and van der Plicht 2007).

Measurement and Calculations

AMS measurements are made by comparing the count rate of ^{14}C from a sample to the count rate in a known-age standard. For activity (counting) measurements, the normalized activity (A) is compared to that of a known standard. In both cases, we can then compare the measured ratio of the sample to a known standard.

Standards

For ^{14}C , we use a primary (SRM-4990B, OXI) and secondary (SRM-4990C, OXII) standard from the US National Institute of Standards and Technology (NIST) to determine radiocarbon dates. The secondary standard is normalized to the consensus value of OXI. The ratio of OXII/OXI is well defined (Mann 1983). Many other well-established secondary standards are also available, which

can be referred back to the primary OXI value (Scott et al. 2007). Some laboratories use their own internal standards and reference them to the primary oxalic acid standards.

Uncertainties

Burr et al. (2007) have summarized how the uncertainties in radiocarbon dates are determined at the Arizona laboratory. There are several potential problems when considering radiocarbon dating uncertainties. For example, radiocarbon dates are quoted with one standard deviation uncertainties by convention, whereas calibrated radiocarbon dates are normally quoted at two standard deviations. Some laboratories estimate additional errors above counting errors from their laboratory procedures (these are always present), but others do not. Often radiocarbon age uncertainties are published, especially by nonspecialists, with little discussion of how they were determined, and uncertainties in reservoir corrections are often neglected. It is therefore important to quote the original “radiocarbon ages” because they are unambiguous assuming they adhere to the definition given above.

Using Calibration Curves

There are a number of programs available for calibration of the “radiocarbon age” to a calendar age. Some good examples easily accessible on the Internet are Calib (www.calib.org) and OxCal (c14.arch.ox.ac.uk/oxcal). The result of applying the calibration to a radiocarbon result can be shown in Fig. 4a, b, where we see the difference between a radiocarbon date of $2,320 \pm 20$ and $2,320 \pm 30$ years. The difference in the precision of the calibration age is due to the structure of the calibration curve.

$\Delta^{14}\text{C}$ Notation

For certain samples, the initial value for modern (1950 AD) will not be the same as the atmosphere. We know that there are offsets in marine samples (e.g., Dumond and Griffin 2002), and there can also be offsets in other samples such as lakes (Yu et al. 2007), where the radiocarbon content of the carbon in the lake may not be “modern” (i.e., at the level of A_0) due to storage or input of old carbon from other sources. Age offsets of this type are described in terms of the difference between the

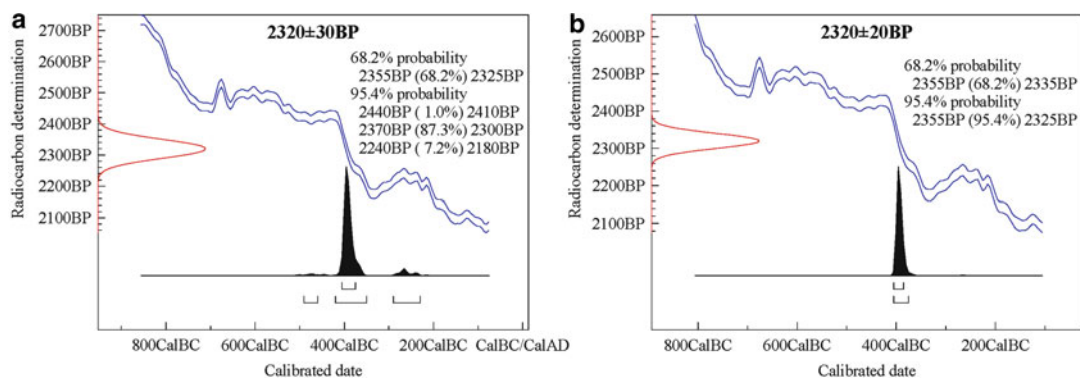


Fig. 4 (a, b) The result of a calibration of a radiocarbon date using the Oxcal calibration program (c14.ox.ac.uk/oxcal) for two values of slightly different precision

radiocarbon content of the reservoir and contemporary atmosphere. This is the age-corrected $\Delta^{14}\text{C}$ value. For sample prior to 1950 AD, $\Delta^{14}\text{C}$ is defined as

$$\Delta^{14}\text{C} = 1,000 \left(\text{Fe}^{\lambda(a)} - 1 \right) \% \quad (7)$$

where a is the absolute age of the material in years before 1950 AD (often stated as calendar years BP in radiocarbon literature), which should be independently obtained. An example of this use is Miyake et al. (2012).

A different situation is the case of a sample containing ^{14}C from after 1950 AD, such as a sample containing bomb ^{14}C . In this case, the true $\Delta^{14}\text{C}$ value should be corrected for the decay of the standard, as the standard has some age relative to the material being studied. This increases F to the correct value.

$$\Delta^{14}\text{C} = 1,000 \left(\text{Fe}^{\lambda(a-1950\text{AD})} - 1 \right) \% \quad (8)$$

In Eqs. 5 and 6, the λ used is 1.21×10^{-4} , representing the true half-life (5,730 years) of ^{14}C .

Marine Reservoir Effects

Stuiver et al. (1986) defined the “marine reservoir effect” as the difference between the measured radiocarbon age and the atmospheric age determined independently at a known time (t):

$$R(t) = {}^{14}\text{C age of marine sample} - {}^{14}\text{C age of atmospheric sample} \quad (9)$$

This correction factor can be determined directly from coexisting marine and terrestrially derived plant material at the same location. The value of R can be related to $\Delta^{14}\text{C}$ by the equation (Burr and Jull 2009):

$$R = 8033 \ln \left(\frac{\frac{\Delta^{14}\text{C}_{\text{atm}}}{1,000} + 1}{\frac{\Delta^{14}\text{C}_{\text{mar}}}{1,000} + 1} \right) \quad (10)$$

Also, Stuiver et al. (1986) introduced the concept of ΔR . It is important to understand the definition of ΔR , to quote from Stuiver et al. (1986), who defined a graphical model for this calculation, “*The difference ΔR in reservoir age of the regional part of the ocean from which the users sample is derived, and the reservoir age of our model ocean, is determined through the use of figure 10A.*”

Stuiver et al. (1986) paper defines the oceanic reservoir age value ΔR as

$$\Delta R = R_{\text{measured}} - R_{\text{exp}} \quad (11)$$

where R_{measured} is the R actually measured in the ocean water and R_{exp} is the expected value derived from the model of Stuiver and Braziunas (1993). It is important to be aware that this is a model-dependent expression. Because this is not always easily established, many authors report R_{exp} as the average oceanic value of R which is 400 years (e.g., Cordero et al. 2003). So, the definition of ΔR (as opposed to R) is dependent on the oceanographic model used. This marine model is now incorporated into the calibration software (e.g., MARINE09, Reimer et al. 2009).

Cross-References

- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Bomb Carbon](#)
- ▶ [Dendrochronology](#)
- ▶ [Paper and Parchment](#)
- ▶ [Plant Macrofossils](#)
- ▶ [U–Th Dating](#)
- ▶ [Varved Sediments](#)

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Accelerator Mass Spectrometry

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Synonyms

[Accelerator dating](#); [AMS](#); [Atom counting](#)

Definition

Accelerator mass spectrometry is a technique that combines a particle accelerator with a mass spectrometer in order to measure very low levels (10^{-16}) of cosmogenic and anthropogenic radionuclides employed for dating purposes.

Introduction

Accelerator mass spectrometry (AMS) is widely used to measure rare isotope ratios of cosmogenic and anthropogenic nuclides. Cosmogenic isotopes are produced through the interaction of cosmic rays with atmospheric molecules, rocks at the earth's surface (Dunai, 2010) and in extraterrestrial settings. AMS is the analytical tool of choice for a range of isotopes used for dating purposes, especially radiocarbon dating and surface exposure dating. Table 1 lists a number of these isotopes, hereafter referred to as *AMS isotopes*. These can potentially be used to date samples from years to tens of millions of years old. The chief advantage of AMS over standard mass spectrometry is that it eliminates molecular interferences using particles with 100 s of keV to 10s of MeV energies. In recent years the technological development of AMS instruments has focused on the production of smaller (<1 MV) machines, which are less expensive to fabricate, require less space, and are easier to maintain than larger machines. This trend has seen an expansion of AMS facilities around the world. Currently there are about 100 active AMS machines worldwide (Kutschera, 2013).

History and Development of AMS

The concept and implementation of AMS date to the late 1970s, when Muller (1977) proposed the idea based on a cyclotron experiment conducted in the 1930s to measure ^3H and ^4He (Alvarez and Cornog, 1939). Muller showed that a particle accelerator could be used as a mass spectrometer to drastically reduce sample sizes and counting times and improve precision and background levels encountered in conventional decay counting of ^{14}C (radiocarbon) and ^{10}Be .

Within months, Nelson et al. (1977) and Bennett et al. (1977) implemented the idea using linear particle accelerators. These measurements were made using relatively large accelerators operating

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Table 1 Isotopes measured with AMS for dating studies and their half-lives

Isotope	Half-life (yr)	Reference
^{10}Be	$1.387 \pm 0.012 \times 10^6$	Korschinek et al. (2010)
^{32}Si	$1.44 \pm 0.11 \times 10^2$	Fifield and Morgenstern (2009)
^{14}C	$5.700 \pm 0.030 \times 10^3$	Kutschera (2013)
^{41}Ca	$9.94 \pm 0.15 \times 10^4$	Jörg et al. (2012)
^{81}Kr	$2.29 \pm 0.11 \times 10^5$	Baglin (2008)
^{36}Cl	$3.013 \pm 0.015 \times 10^5$	Nica et al. (2012)
^{26}Al	$7.18 \pm 0.18 \times 10^5$	Kutschera (2013)
^{53}Mn	$3.7 \pm 0.4 \times 10^6$	Honda and Imamura (1971)
^{129}I	$1.57 \pm 0.04 \times 10^7$	Tendow (1996)

with terminal voltages of 7 and 8 MV and particles ranging from 35 to 40 MeV. Over the next several years, smaller (3 MV), purpose-built AMS instruments began to appear. Since that time, smaller instruments have been introduced and the trend toward smaller and smaller machines continues. Nowadays, especially for ^{14}C , systems are being designed with accelerator voltages as low as 200 kV. Such systems, designed at ETH Zürich, have already been installed in several laboratories (Suter, 2010). While further developments may reduce this voltage further, some nuclides such as ^{10}Be and ^{36}Cl still require higher energies to eliminate isobaric interferences and maintain high transmission.

AMS Design

Accelerator mass spectrometers all share the same basic components: (1) ion source, (2) injection (low-energy) magnet with an electrostatic field switching device (bouncer), (3) particle accelerator and stripper, (4) high-energy particle filters for magnetic and electrostatic separation, and (5) a particle detector (Fig. 1). All designs of AMS use negative ions that are produced in an ion source and are then accelerated through a potential of up to 50 kV, focused into a particle beam and sent through an injection magnet. The injection magnet performs an initial separation of beams of different masses. However, molecular ions are still present at these lower energies. After the ions pass through the injection magnet, they are further accelerated by the voltage on the AMS terminal. The terminal contains a “stripper” which can be a gas canal or thin film. When the high-energy ions pass through the stripper, molecules are dissociated and the injected particles lose electrons to become positive. In tandem accelerators the resulting positive particles continue to be accelerated in the same direction, back to ground potential. One design, the simplified “single-stage AMS,” places the ion source at the accelerating potential and the detectors are at ground potential. In this device the high-energy ions are analyzed on their way to the detector using a variety of magnetic and electrostatic filters. The ion beam is focused along the path from the ion source to the detector, using different combinations of Einzel, quadrupole, and gridded lenses, accompanied by collimating slits and electrostatic steering devices. The choice of lenses and their placement depend on the design and model of each AMS and vary considerably. The detection system can consist of solid-state devices (surface-barrier detectors) or gas-filled detectors, where further analysis of ion energy and energy loss in a gas can be measured. AMS detectors generally can identify ions by both mass and atomic number, allowing for complete separation of isobaric interferences (Litherland et al., 2010).

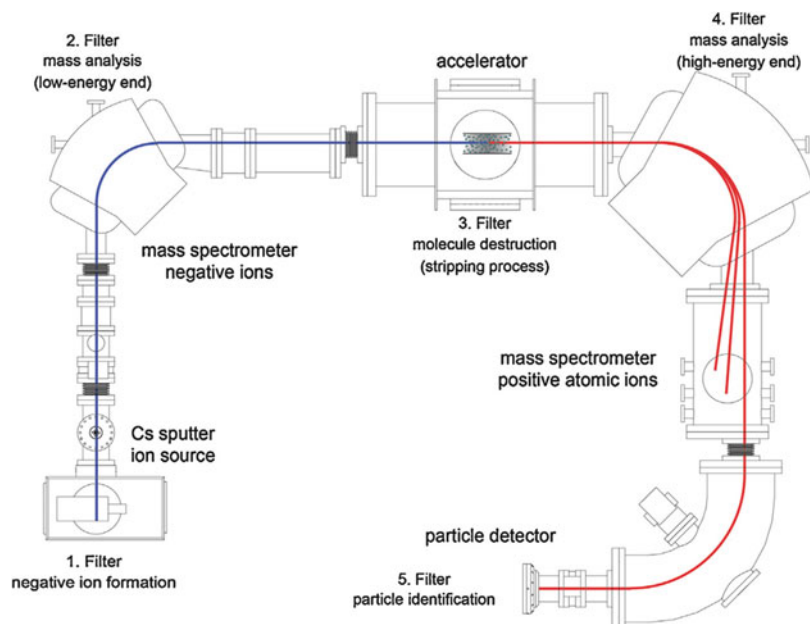


Fig. 1 Typical AMS design (From Sinal, 2013)

Dating Applications

AMS dating applications are primarily concerned with the measurement of cosmogenic radionuclides, but also include applications using anthropogenic isotopes. Radiocarbon was the first cosmogenic nuclide to be widely applied as a dating tool using AMS (Elmore and Phillips, 1987). Most radiocarbon is produced in the atmosphere as a result of cosmic ray interactions with atmospheric molecules. These reactions supply thermal neutrons that produce radiocarbon through the $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$ reaction. Atmospheric radiocarbon rapidly spreads into terrestrial and marine environments around the globe along a variety of organic and inorganic pathways. When a pathway is cut off, for example, when an organism dies, its radiocarbon content begins to drop as it decays away at a known rate. An AMS radiocarbon date can be determined on such material by comparison between the measured radiocarbon content in the sample and in a standard representing the atmospheric value. The limit of the AMS radiocarbon dating technique is about 55 kyr. Anthropogenic (non-cosmogenic) radiocarbon can also be used for dating. Bomb carbon introduced into the atmosphere through aboveground nuclear weapon testing in the late 1950s and early 1960s produced a spike which has been widely exploited for dating samples from the last 60 years (see entry “► Bomb Carbon” by Burr in this volume). In this case excess radiocarbon, above the expected atmospheric value, is determined with AMS. A third production pathway for radiocarbon is through spallation reactions within rocks and meteorites. This radiocarbon is well suited to in situ dating (discussed next) and to determine the terrestrial ages of meteorites (Jull, 2001).

In situ dating is concerned with the buildup of cosmogenic nuclides that occurs when a geologic surface is exposed to cosmic rays (Gosse and Phillips, 2001). Some examples of applications are to determine the age of a lava flow, or the age of a glacial deposit marking the retreat of the glacier. AMS is a truly pioneering method in the case of in situ studies because the sample size requirements, sensitivity, and precision of the AMS technique made in situ dating possible. Most in situ dating studies measure ^{10}Be , ^{14}C , ^{26}Al , and ^{36}Cl . In situ dating has advanced rapidly since the introduction of AMS and has seen a steady expansion of applications. Examples include (1) surface exposure

dating on the earth and moon, (2) determination of erosion and weathering rates, (3) burial dating, and (4) determination of the terrestrial ages of meteorites. The goal of surface exposure dating is to date fresh rock or soil surfaces that have been continuously exposed to cosmic rays since they formed and ideally have experienced only minor erosion (Granger et al., 2013). In situ isotopes can also be used to infer erosion and weathering rates when the age of a surface is known independently. In this case, the amount of material removed by both physical and chemical erosion can be assessed. When two cosmogenic isotopes are measured in the same rock, it can also be possible to determine both surface exposure age and erosion rate (Granger et al., 2013). A recent addition to this group of in situ isotopes is ^{53}Mn , which has been measured in several laboratories and has been used to study both terrestrial and extraterrestrial samples.

Another AMS isotope commonly used for dating applications is ^{129}I . Like radiocarbon, both cosmogenic and anthropogenic sources of ^{129}I can be used for dating. ^{129}I is particularly useful for dating brines and evaporite deposits (Fabryka-Martin et al., 1984) because iodine is very soluble and becomes concentrated in these materials. ^{129}I has a very long half-life (1.57×10^7 years) and has been used to date brine samples as far back as the Miocene (Tomaru et al., 2009). Iodine is a near-conservative element in groundwater and has showed promise as a method suitable for dating young water (Schwehr et al., 2005).

The remaining AMS isotopes given in Table 1 (^{32}Si , ^{41}Ca , ^{81}Kr) are less widely studied but have potential as isotopic chronometers. ^{32}Si has long been recognized as a potentially useful radioisotope for dating oceanographic samples (Lal et al., 1960), but poses significant analytical challenges, in part due to its low abundance. Fifield and Morgenstern (2009) have demonstrated the feasibility of dating glacial ice with AMS measurements of ^{32}Si . The potential for ^{41}Ca has also been long recognized (Paul et al., 1985), but is a challenging isotope to measure. ^{41}Ca has been measured to determine cosmic ray exposure ages of meteorites (Herzog et al., 2011). The strictly conservative nature of krypton in groundwater makes ^{81}Kr a valuable isotope in determining the residence time of ancient groundwater. Collon et al. (2000) developed a specialized sample processing technique to extract krypton from groundwaters of the Great Artesian Basin in Australia and determined ages from about 2 to 4×10^5 years.

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Extraterrestrial Materials (K–Ar/Ar–Ar)

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Definitions

Potassium-argon (K–Ar) dating is a technique of finding the ages of rocks based on the decay of ^{40}K to ^{40}Ar . Argon-argon (^{40}Ar – ^{39}Ar , or just Ar–Ar) dating is a type of potassium-argon dating in which a sample is irradiated with neutrons, converting a fraction of the atoms of ^{39}K , the most abundant isotope of potassium, into ^{39}Ar , enabling both the potassium abundance and the ^{40}Ar abundance to be measured with a single noble gas mass spectrometer (McDougall and Harrison 1999). The extraterrestrial materials to which the potassium-argon and argon-argon techniques have been applied include only meteorites and samples returned from the surface of the Moon by either the American Apollo astronauts or the Russian Luna robotic sample-return missions – age determinations based on the decay of radioactive isotopes have never been attempted in-situ on any planetary surface, but several concepts based on the K–Ar technique have been proposed since 2000.

Introduction

The potassium-argon system, which is at the heart of both K–Ar and Ar–Ar dating, is notable among the major geochronology systems with respect to easy diffusion of the daughter product, ^{40}Ar . As a result, it can be applied in cases where a rock is heated, but not to a high enough temperature for a long enough period of time for other systems to be reset. It is this quality that makes it very useful for impact age determinations.

The rarest of the three naturally-occurring potassium isotopes, ^{40}K , decays to either ^{40}Ca or ^{40}Ar , with a total half-life of 1.25 Ga (Renne et al. 2011). Although the majority of the decays are to Ca, it is the branch involving Ar that is far more widely used as a geochronometer, because Ar is far rarer than Ca.

The possibility of using the K–Ar system for age determinations was discussed in the 1940s, and heavily implemented as K–Ar dating in the 1950s. Although the possibility of something like Ar–Ar dating was discussed late in that decade, the first real Ar–Ar experiment was performed on the Bruderheim meteorite in the mid-1960s (Merrihue and Turner 1966). It was quickly applied to other meteorites, and when the Apollo lunar samples were returned just 3 years later, the technique was already mature enough that it was used heavily.

Because Ar does not engage in chemical bonds, a silicate melt will tend to lose its Ar, so most rocks contain little or no Ar when they form. However, Ar diffuses only sluggishly through solids, so ^{40}Ar will then build up, and in an extremely simple system, a K–Ar age records the length of time since the rock was formed. However, Ar diffusion is temperature-dependent – if a rock is heated up,

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Ar will begin to escape long before the rock is melted. How much Ar is lost depends on the diffusion characteristics of the host mineral as well as the time and temperature history of the rock, so in a rock that has been heated at some time after it cooled, some or all of the radiogenic (decay-produced) ^{40}Ar will have been lost, and the K–Ar age will be between the formation age and the length of time since the reheating event. Or, if the time-temperature history is sufficient, the rock can lose all of its radiogenic ^{40}Ar in a thermal event and the K–Ar age will record the time since that event. Actually, it will record the time since the rock was last at a temperature high enough to lose Ar by diffusion, a temperature that depends on the diffusion characteristics of the mineral and on the cooling rate, but is typically a few hundred degrees Celsius. Diffusion characteristics have been determined for many minerals, and this type of calculation is at the heart of “thermochronology” techniques (McDougall and Harrison 1999).

In the most common version of Ar–Ar dating, the irradiated sample is heated to progressively higher temperatures, and the gas released at each step is analyzed. This sort of step-wise heating approach has several advantages over classical K–Ar dating. First, most of the release is through diffusion, so mineral sites from which diffusion occurs more readily, because of the grain size, the diffusion characteristics of the mineral, or the proximity of the site to the edge of the rock or to a fast-diffusion pathway, are degassed more readily. This makes it possible to distinguish Ar from different mineral sites. In addition, the diffusion characteristics can be determined in the experiment itself. Finally, in a situation where the rock has been only partially degassed, or where some mineral sites have been degassed, but not others, different steps will give different ages, so it is possible to determine that it is a complex system, and possibly even to sort out some of the complexity. The most detailed review of Ar–Ar ages of meteorites is given by Bogard (2011).

The heating caused by impact cratering often leads to a complex system. For one thing, the heating can be to a very high temperature but for a very brief period of time, often leading to only incomplete Ar degassing. Furthermore, the time-temperature history can lead to some counter-intuitive results. For example, a glassy vein of impact melt material may retain more Ar than unmelted material nearby (McConville et al. 1988), or a mineral in which diffusion is slower at low temperatures but faster at high temperatures may suffer more Ar loss than one that degasses more readily at laboratory temperatures (Cassata et al. 2011).

Ordinary Chondrite Metamorphism

Ordinary chondrites, the most common types of meteorites, can be divided into three groups, presumably representing different parent asteroids, based on their chemical composition. However, within each group, the ordinary chondrites can be divided into metamorphic types, reflecting the amount of high-temperature processing (such as chemical equilibration and mineral recrystallization) they have experienced. A very simple model to explain the metamorphic types envisions all the meteorites of a single group on a single parent asteroid that heats up and then slowly cools by radiating its heat away from the surface. In this case, the rocks near the surface would experience the lowest heating, and would cool past any particular temperature first, while those in the center would be heated the most and take the longest to cool down. In this case, the Ar–Ar ages, which reflect the time at which the rock cooled past a particular temperature, should be younger for samples that are more highly metamorphosed, reflecting this “onion-shell” structure. An initial study of ordinary chondrites did not find such a relationship overall (Turner et al. 1978). A later study, focused on a single type of ordinary chondrites, the H (high-iron) chondrites, and concentrated on meteorites with little evidence for the complicating effects of impact heating, and found

the predicted correlation between age and degree of metamorphism (Trieloff et al. 2003), both for Ar–Ar ages and Pb–Pb ages, with Ar–Ar ages extending over a ~0.1 Ga period. This suggests that the H chondrite parent body, at least, may have had such an onion-shell structure. However, experiments on the other two groups of ordinary chondrites have not shown such a relationship (Dixon et al. 2004; Turner et al. 1978).

Determining the Ages of Lunar Impact Craters

For most of its history, the dominant geological process on the surface of the Moon has been impact cratering. There are enough craters that it is possible to build up a detailed relative chronology based on the density of impact craters on a surface. Such relative chronologies can be constructed for the surfaces of many planets and moons, but only for the Moon do we have samples on which we can determine ages based on isotopic systems, so the Moon and its cratering rate serve as a standard for the determination on other surfaces (see “► [Planetary Surfaces \(Cratering Rates\)](#)”). The primary way by which ages of craters are determined is Ar–Ar dating, although other techniques can sometimes be applied (Stöffler and Ryder 2001).

Within 4 years of the first samples having been returned from the Moon, it was clear that there is a concentration in the Ar–Ar ages of Apollo samples at about 3.9 Ga (Turner et al. 1973). Almost simultaneously, Tera et al. (1974) determined that many of the Apollo samples, from various sites, appear to have uranium-thorium-lead ages that were disturbed at about the same time. This led Tera et al. (1974) to suggest that there had been a “lunar cataclysm,” a large number of cratering events on the Moon in a relatively short interval of time. Subsequent research has shown that there were events both earlier (Fernandes et al. 2013) and later (Cohen et al. 2005) than the ~3.9 Ga spike in ages seen in the early Apollo data. However, evidence from asteroidal meteorites also suggests that the impact cratering rate in the Solar System was higher between ~4.1 and 3.4 Ga than either earlier or later (see below).

In parallel with the chronology studies, investigations into early Solar System orbital dynamics revealed a plausible mechanism for a cataclysm, involving the migration of the orbits of Jupiter and Saturn (Gomes et al. 2005). As more details of the complexity of the impact cratering history have been revealed, the orbital dynamics models have become more complex, as well (Morbidelli et al. 2012).

Impact Ages of Asteroidal Meteorites

Impact ages have been determined for more than 100 meteorites from asteroids (Bogard 1995; Swindle et al. 2013), including all three groups of ordinary chondrites, the HED meteorites that are presumed to come from the asteroid 4 Vesta, the mesosiderites (a kind of stony iron meteorite) and the IIE iron meteorites. The HED meteorites predominantly give impact ages of 3.4–4.1 Ga, although the impact crater distribution on Vesta observed by the Dawn spacecraft has been interpreted as demonstrating a massive impact event at ~1 Ga (Schenk et al. 2012), an unresolved puzzle. Most other meteorite groups are also roughly consistent with the lunar record, with more impact ages of 3.4–4.1 Ga than either before or after, except for the most recent 1 Ga. In the recent past, the best recorded impact is a large event that affected the L (Low-iron) chondrite parent body at 0.47 Ga, an event that is also recorded in fossil meteorites found in terrestrial quarries of that age

(Schmitz et al. 2001). It is not clear whether the higher number of recent ages reflects an increase in cratering rate or a short average survival lifetime.

Ages of Martian Meteorites

Argon-argon dating has also been applied to meteorites from Mars, although the most important result was not an age. In an attempt to determine the age of Elephant Moraine A79001, one of a group of igneous meteorites with remarkably young crystallization ages based on other chronometers, D. D. Bogard and P. Johnson found that the apparent age of some samples was greater than the age of the Solar System, unless the data was corrected for a “trapped” component with a very large ratio of ^{40}Ar to ^{36}Ar . Further study revealed that the samples with the high ^{40}Ar contents were also enriched in the other noble gases (neon, krypton, and xenon), and had relative abundances of the noble gases, as well as key ratios of isotopes of Ar and Xe, that matched measurements of the Martian atmosphere by the Viking spacecraft in the 1970s (Bogard and Johnson 1983). This was taken as confirmation of an earlier suggestion that this group of meteorites indeed comes from Mars. High amounts of argon, apparently trapped either from the atmosphere or from magmas, are found in many of the Martian meteorites, making it difficult to determine accurate argon-argon ages (Bogard et al. 2009). However, on those meteorites where ages can be determined, it appears that the rocks are relatively young, mostly 1.3 Ga or younger (Nyquist et al. 2001), and were not subjected to high temperatures on Mars (Weiss et al. 2002).

In-Situ K–Ar Dating

Several concepts for performing K–Ar dating in situ on planetary surface, have been suggested (Cohen et al. 2013; Farley et al. 2013; Swindle et al. 2003; Talboys et al. 2009), but none has yet flown on a spacecraft. Mars is a particularly appealing target, because the relative ages of Martian surfaces can be determined by geological superposition relationships or by the relative abundance of impact craters, but the absolute ages are poorly known. Ar–Ar dating cannot be applied because of the high neutron fluences required, but metamorphism is not expected to occur, so K–Ar dating might be expected to date formation ages.

Summary or Conclusions

Potassium-argon dating, specifically the Ar–Ar variant, has been widely applied to extraterrestrial samples. The relative ease of diffusion of Ar, compared to the elements involved in other isotopic dating techniques, has made Ar–Ar the most widely used system to determine the timing of heating events, particularly those from impact cratering.

Cross-References

- [Meteorites, Uranium-Lead](#)
- [Noble Gas Mass Spectrometer](#)
- [Planetary Surfaces \(Cratering Rates\)](#)
- [Thermochronology, Meteorites](#)
- [Uranium-Lead, Extraterrestrial, Planetary Materials](#)

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Radioluminescence (RL)

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Synonyms

[Infrared radiofluorescence](#); [Infrared radioluminescence](#); [IR-RF](#)

The radioluminescence (RL) phenomenon is based on the emission of fluorescent light at a wavelength range of 865 nm occurring when potassium (K-) feldspar grains are exposed to a radioactive source (e.g., Trautmann et al. [1998](#); Erfurt et al. [2003](#)). The ionization leads to electron transfers from an excited state to the ground state of the electron center (Trautmann et al. [2000](#)), and RL is emitted while electrons are captured in free optically active traps. RL is therefore not linked to recombination centers and reflects the charge density within electron traps (Trautmann [2000](#)). RL is most likely related to electron transitions in Pb^+ centers (Erfurt [2003](#)). Contrary to the luminescence signal, the RL signal decreases with irradiation time until a saturation limit is reached, and the RL signal can be increased by exposing the K-feldspars to light <500 nm (>2.5 eV).

The radioluminescence phenomenon can be used for dating applications. Infrared radioluminescence or infrared radiofluorescence (IR-RF) dating is a method which can be used to determine the depositional age of Quaternary sediments (e.g., Trautmann et al. [1999](#); Krbetschek et al. [2000](#)) and therefore provides an alternative to the *luminescence dating* method. As IR-RF dates the last sunlight exposure of feldspar grains before burial, a sufficiently long sunlight exposure of the investigated material during transport (e.g., aeolian, fluvial) is mandatory.

The saturation dose of the IR-RF is at about 1,200–1,500 Gy (Erfurt and Krbetschek [2003](#)), and with an IR-RF single-aliquot regenerative-dose dating protocol, it was possible to date sediments >600 ka (Wagner et al. [2010](#); Lauer et al. [2011](#)). However, bleaching properties, and sensitivity changes of the IR-RF signal in between measurement cycles, have to be checked to obtain accurate age estimates (Buylaert et al. [2012](#)).

Cross-References

► [Luminescence Dating](#)

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Rb–Sr Geochronology (Igneous Rocks)

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Synonyms

Mica chronology; Mica dating; Rb–Sr dating; Sr dating; Sr geochronology

Definition

Application of the radioactive decay of ^{87}Rb to ^{87}Sr to determining the age of crystallization of igneous rocks.

Introduction and Background

Both rubidium (Rb) and strontium (Sr) are large ion lithophile elements and over the course of Earth history have become relatively concentrated in crustal lithologies, e.g., gneisses and granites, and sediments derived from these. Because of this, application of the Rb–Sr decay scheme was one of the first radiometric dating systems used to determine the age of rocks and remains a widely used system for dating geological units formed at relatively high temperatures, in particular volcanic, plutonic, and metamorphic rocks formed in the crust. Relatively low closure temperatures for commonly used minerals and susceptibility for disturbance of Rb and Sr complicate the use of the system as a geochronometer, and application of methods such as U–Pb in zircon is often preferred to yield more reliable age information.

Age determination with the Rb–Sr system revolves around the construction of an isochron using minerals or rocks with variable Rb–Sr ratios. Igneous rocks form by the cooling, crystallization, and solidification of magmas. During crystallization, different minerals form depending on pressure and temperature and the composition of the magma. Elements present at trace concentrations ($<1,000$ ppm) in magmas will not normally form their own minerals but will instead be incorporated into minerals by substituting for major elements with similar ionic radii and charge. Rb is monovalent with an ionic radius similar to K^+ so will tend to be concentrated in K-rich minerals, whereas Sr is bivalent and substitutes for Ca^{2+} in mineral lattices. Minerals with high K contents (e.g., biotite, alkali feldspar) will therefore have high Rb/Sr, whereas Ca-rich minerals (e.g., plagioclase feldspar, clinopyroxene, calcite, apatite) will have low Rb/Sr. During construction of an isochron, various mineral phases with variable Rb/Sr ratios are separated from a rock. These minerals are then dissolved and Rb and Sr purified by ion exchange chromatography and analyzed for their Rb and Sr concentrations and Sr isotope composition, typically by thermal ionization mass spectrometry (TIMS). Mineral selections are made so as to aim for as wide a range in Rb/Sr as

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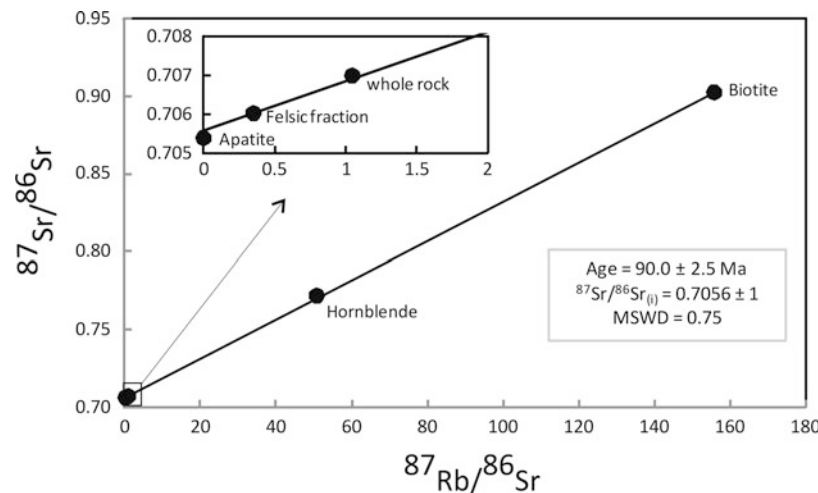


Fig. 1 A combined mineral whole rock isochron for the Habu Granodiorite in Japan; the inset shows the compositions of the whole rock powder, a felsic mineral fraction (mostly feldspar and quartz), and three apatite separates (Data from Tsuboi and Suzuki 2003). $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$ is the intercept of the isochron with the Y-axis and represents the initial isotopic composition of the magma at the time of emplacement. MSWD (mean square of weighted deviates) is a statistical parameter describing the degree of fit of the data points to a straight line

possible. A whole rock composition (representing an average of all the minerals present in the rock) is also often included in the age determination.

At the time of crystallization, the minerals inherit the original Sr isotope composition of the parental magma. With time the ^{87}Rb in the minerals will decay to ^{87}Sr , such that K-rich (Rb-rich) minerals will become progressively more radiogenic (higher $^{87}\text{Sr}/^{86}\text{Sr}$) with time, whereas the amount of ingrowth in the Rb-poor minerals will be lower or, in the case of Rb-free minerals, absent. For samples that behave as a closed system, plotting the measured $^{87}\text{Sr}/^{86}\text{Sr}$ of the different mineral phases versus their $^{87}\text{Rb}/^{86}\text{Sr}$ composition (isochron diagram) will define a line (an isochron) with a slope that is proportional to the age of the rock (see Fig. 1). The age of the rock can then be calculated using the equation:

$$t = \frac{1}{\lambda} \ln(1 + \text{slope})$$

The intersection of the isochron with the Y-axis (or alternatively analysis of a Rb-free phase) provides the initial Sr isotopic composition of the system $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$, a parameter that is useful to geochemists for understanding the geological history of the source rocks that melted to generate the magma. Chemical differentiation of the Earth over its history due to partial melting has resulted in the mantle having relatively low Rb/Sr, and thus, over time, it has evolved to relatively unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (ca. 0.7035). In contrast, the continental crust has relatively high Rb/Sr and has thus evolved to have highly variable and typically radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (e.g., >0.710). As Sr isotopic compositions are not modified by processes such as melting and crystallization, these signatures can be used to identify the source(s) of magma and to identify processes such as crustal contamination of mantle-derived magmas.

An example of a mineral isochron constructed for the Habu Granodiorite in southwest Japan is shown in Fig. 1. Various mineral phases were separated from the rock and, together with a whole rock powder and a felsic mineral fraction (dominated by feldspar), were analyzed for their Sr

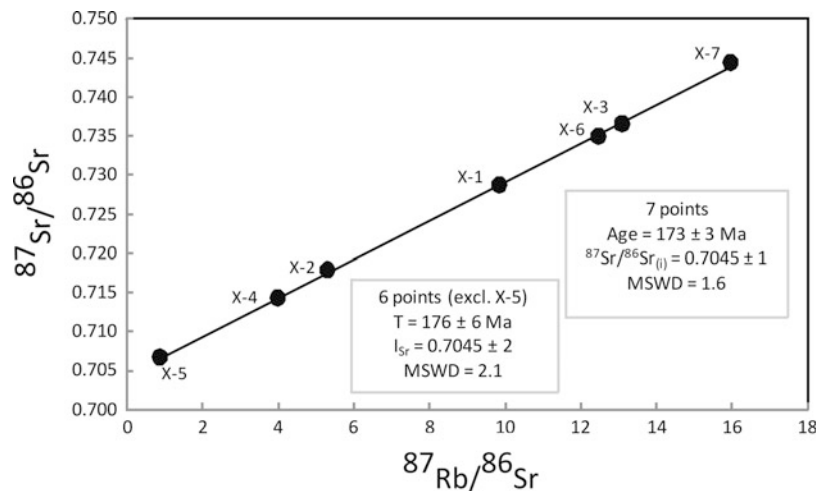


Fig. 2 Rb–Sr whole rock isochron for the Xinhuatun Granite, northeastern China, redrawn from Wu et al. (2003). Two ages are presented, one excluding sample X-5 which is a microgranular enclave and may not be directly related to the magmatic system; both ages are identical within error

isotopic composition and Rb and Sr concentration. Biotite, with a high Rb/Sr, has evolved with time to have a high $^{87}\text{Sr}/^{86}\text{Sr}$, whereas the felsic mineral fraction with a lower Rb/Sr has a much less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$. The apatite analyses fall off the isochron and were not included in the age calculation as the aim of this study was to assess their suitability for determining the initial isotopic composition of a magma.

In order to obtain meaningful age information from a mineral isochron, three fundamental assumptions must be fulfilled:

- The minerals all formed in equilibrium with each other.
- The minerals all formed from a reservoir of homogeneous isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$).
- The minerals have been a closed system (i.e., not been subject to thermal or chemical disturbance) subsequent to crystallization.

It is possible to assess the validity of these assumptions statistically through the degree of fit of the analyses to a straight line regression (MSWD) and in the extrapolated error on the initial isotopic composition.

A Rb–Sr isochron for igneous rocks can also be constructed using whole rock compositions. Magmas become more evolved (i.e., enriched in SiO_2) during crystallization through the process of fractional crystallization, where minerals crystallize and become isolated from the surrounding residual magma. During fractional crystallization, Rb generally behaves as an incompatible element (preferring to remain in the melt phase rather than going into the crystalline phase). Therefore, Rb concentrations will increase in residual melts as the magma progressively crystallizes and becomes more evolved, at least until generally late-stage K-bearing minerals such as alkali feldspar and biotite begin to crystallize. In contrast, plagioclase feldspar, the major reservoir for Sr in an igneous system, crystallizes over a broad range of temperatures, and therefore, Sr concentrations in residual magmas will tend to decrease with increasing differentiation. As a consequence, Rb/Sr will generally increase in residual melts with increasing fractional crystallization and evolution. A series of whole rock samples with variable Rb/Sr can thus be analyzed from a single magmatic series and plotted on an isochron diagram to yield an age. An important assumption in constructing whole rock Rb–Sr isochrons is that the magma crystallized as a closed

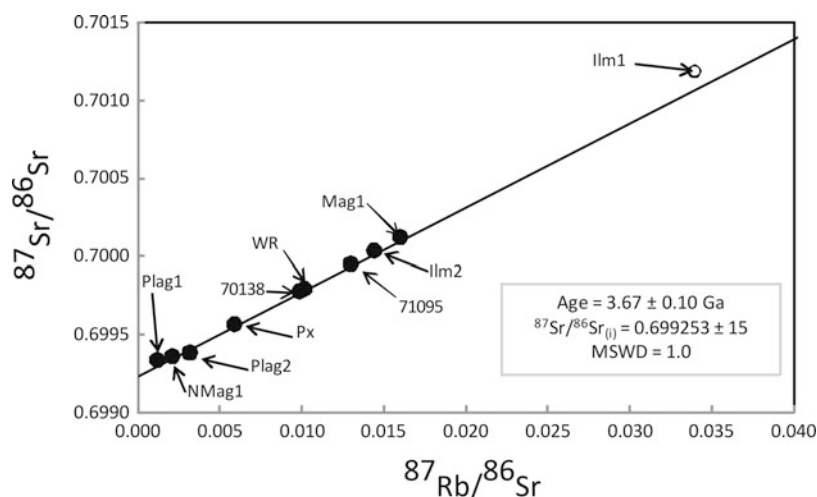


Fig. 3 Rb–Sr mineral isochron for a lunar basalt, redrawn from Paces et al. (1991). The different minerals analyzed are plagioclase feldspar (Plag1 and Plag2), ilmenite (Ilm1 and Ilm2), and pyroxene (Px). Also included are a nonmagnetic mineral fraction (NMag1) dominated by plagioclase and pyroxene, a magnetic mineral fraction (Mag1) dominated by ilmenite and magnetic pyroxene, a whole rock powder (WR), and whole rocks of two additional samples (70138 and 71095). Ilm1 is not included in the regression line calculation

system, that is, there was no input from external sources such as contamination by the surrounding country rock, and thus, all rocks crystallized from a magma with a homogeneous initial isotopic composition. An example of a whole rock isochron based on a sequence of variably evolved rocks from a granitic pluton in China is shown in Fig. 2. The studied pluton outcrops over an area of 160 km² and ranges in composition from granodiorite, through monzogranite, to syenogranite and granophyres and is considered to have evolved by closed system fractional crystallization.

In some cases, it is possible to generate Rb–Sr ages are within error when realistic model ages by analysis of a single, highly radiogenic mineral phase; in fact, this is how the Rb–Sr dating system was first developed. Minerals such as biotite and alkali feldspar with high Rb/Sr will evolve to extremely radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (values >3) in relatively old rocks. At such radiogenic compositions, extrapolation to an assumed and geologically reasonable initial $^{87}\text{Sr}/^{86}\text{Sr}$ (e.g., between values of 0.7 and 0.75) results in minimal change in the isochron slope and thus enables calculation of a model age based on a single data point. For example, alkali feldspar from the Illímaussaq Intrusion in southern Greenland has a measured $^{87}\text{Rb}/^{86}\text{Sr}$ of 407.1 and $^{87}\text{Sr}/^{86}\text{Sr} = 7.4727$. If an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70 is assumed, this results in a calculated age of 1,161.9 Ma, whereas assuming an initial composition of 0.71 produces an age of 1,160.2 Ma; both ages are within error when realistic analytical errors are applied to the measurements (Waight et al. 2002).

Rb–Sr geochronology of igneous rocks is most often applied to evolved lithologies (e.g., rhyolites and granites) as their evolved nature promotes crystallization of the high-K (and Rb) phases ideally suited for dating. Application to mafic rocks is more limited as the rocks themselves, and the minerals that crystallize from them, have limited and generally low Rb/Sr. Nevertheless, it is possible as is illustrated, for example, in the study by Paces et al. (1991) on Apollo 17 lunar basalts, where a Rb–Sr mineral isochron yielded a Rb–Sr age of 3.67 ± 0.10 Ga, in good agreement with a Sm–Nd mineral age on the same material, despite a variation in $^{87}\text{Rb}/^{86}\text{Sr}$ of only 0.001–0.02 (Fig. 3).

The Rb–Sr system has been invaluable in determining the ages of ultramafic rocks such as ► **U-Pb, Rb-Sr, kimberlite**, which are the ultimate source of most of the world’s diamonds, and the related ultramafic lamprophyres. These rocks are amenable to Rb–Sr dating because, despite their

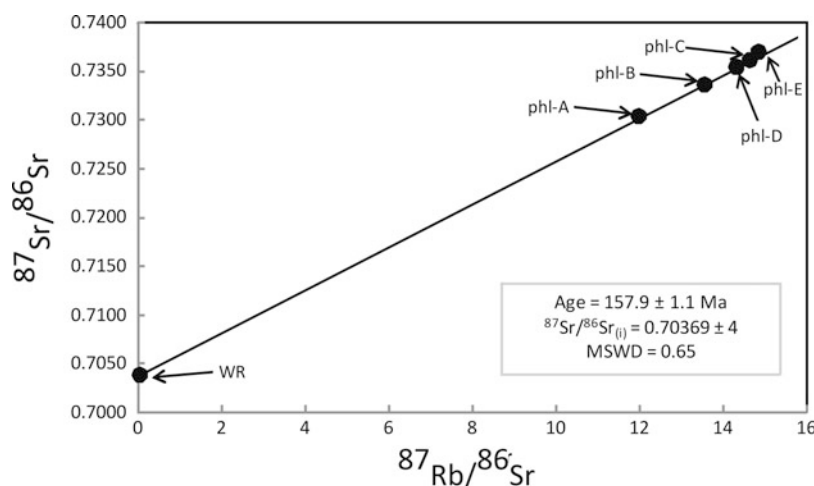


Fig. 4 Rb–Sr isochron for an aillikite dike from West Greenland, comprising five phlogopite phenocrysts (phl-A to phl-E) and a whole rock analysis (Reproduced with permission from Tappe et al. (2009))

very primitive compositions, they can crystallize significant quantities of phlogopite, the Mg-rich end-member of the biotite group of minerals with high Rb/Sr (Heaman 2013; this volume). In contrast, bulk rock kimberlite compositions have relatively low Rb/Sr. This difference between bulk rock and phlogopite Rb/Sr was utilized in the study of Tappe et al. (2009) who dated an ultramafic lamprophyre (aillikite) from Greenland by analyzing five phlogopite phenocrysts and a bulk rock to yield a well-defined Rb–Sr age of 157.9 ± 1.1 Ma (Fig. 4), in good agreement with U–Pb perovskite dates obtained on related aillikite dikes from the same region.

Chemical Disturbance

An important source of error in Rb–Sr dating of igneous rocks is post-crystallization disturbance, particularly in the presence of fluids. Both Rb and Sr are large ion lithophile elements and thus relatively mobile in fluids during, for example, hydrothermal alteration and weathering. The ^{87}Sr produced by radioactive decay of Rb is generally not strongly bound into the crystal structure of the host mineral and thus can be relatively easily mobilized. If this occurs, it will modify the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the investigated phase and potentially move it away from the ideal isochrons, increasing the error on the calculated age or erasing any original age information.

Closure Temperature

All geochronological systems are controlled by closure or blocking temperatures, the temperature at which a mineral system becomes closed to diffusional loss of radiogenic daughter atoms and therefore can begin to accumulate the radiogenic isotopes produced by decay and record age information. In addition to temperature, closure temperatures are also constrained by the diffusivity of the elemental species involved, cooling rates, crystal size, as well as the presence or absence of fluids and tectonic strain.

The closure temperatures for common materials investigated using the Rb–Sr system are relatively well known and are typically relatively low. The high Rb–Sr minerals are most important in constraining geochronological data, and muscovite is typically considered to have a closure temperature for the Rb–Sr system at ca. 500 °C and biotite at ca. 300 °C (Dodson 1973; Villa 1998). Alkali feldspar is less well constrained with a closure temperature of around 475–575 °C (Giletti 1991). In rapidly cooled igneous systems, Rb–Sr ages can be considered to be crystallization ages and generally agree with other geochronological systems with higher closure temperatures (e.g.,

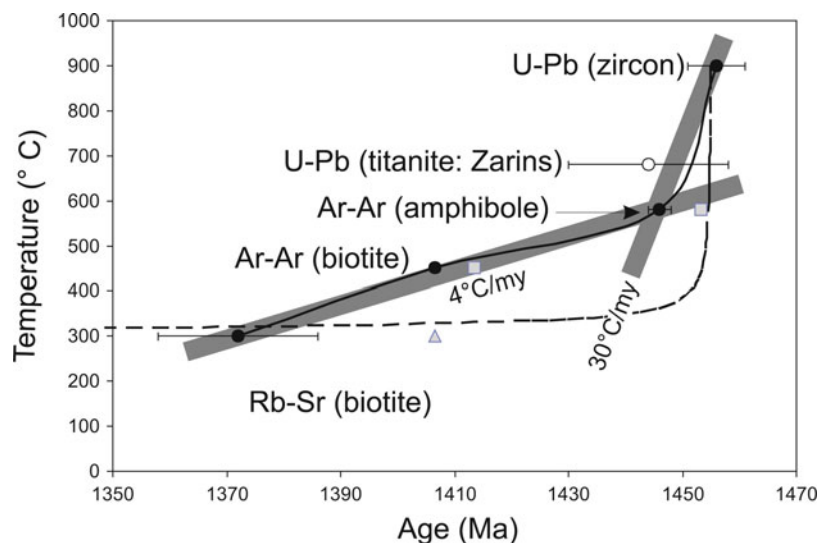


Fig. 5 Geochronological data using various minerals and isotopic systems for the Rønne Granite (Bornholm, Denmark). The *dashed line* is a cooling curve assuming all heat loss is via one-dimensional heat conduction from the intrusion depth (10 km) toward the surface. The *gray symbols* represent various permutations of closure temperatures and decay constants for the ^{40}Ar - ^{39}Ar system (Reproduced with permission from Waight et al. (2012))

U–Pb in zircon). However, in slowly cooled systems this is not the case, for example, the U–Pb zircon system (closure temperature ca. 900 °C) yields an age of $1,456 \pm 5$ Ma for the Rønne Granite (Bornholm, Denmark), yet biotite from the same sample yields Rb–Sr model and two-point isochron ages of about 1,370 Ma and indicates either slow cooling or subsequent disturbance of the Rb–Sr system (Fig. 5). Similarly, the Rb–Sr mineral age presented in Fig. 2 is ca. 10 Myr. younger than U–Pb zircon on the same rock, a discrepancy also attributed to slow cooling by Wu et al. (2003). Age determinations from multiple geochronometers based on different minerals and isotopic systems can thus be used to determine a cooling history for a region. One important consequence of the different closure temperatures for Sr isotopes in various minerals is that slow cooling may result in different minerals passing through their closure temperatures at different times, causing scatter on isochron diagrams. While minerals with higher closure temperatures typically behave as closed systems, other minerals will still be open to diffusional exchange and ongoing radioactive decay prior to closure; thus, the minerals will not have crystallized from a homogeneous reservoir (e.g., Giletti 1991). Similarly, relatively low-temperature thermal disturbances may cause open system behavior and diffusional exchange of elements in some mineral systems, resetting the isotopic systematics and thus erasing any information on the original crystallization age of the magma. However, the low closure temperature for biotite especially has been particularly useful for dating metamorphic events.

Summary

The preferential incorporation of Rb (following K) or Sr (following Ca) into different mineral structures, as well as their differing behaviors during closed system evolution of magmas by fractional crystallization, results in a wide range in Rb/Sr in mineral and whole rock compositions. The radioactive decay of ^{87}Rb to ^{87}Sr can then be exploited to generate an isochron and yield age information about a magmatic system, providing all the analyzed materials crystallized from

a homogeneous parental melt, and the system has not been subsequently thermally or chemically disturbed. Some caution is required when applying the Rb–Sr chronometer to igneous systems; evaluation of the mobility of elements (especially Rb) and whether the strontium isotopic composition has been compromised by fluids (e.g., hydrothermal alteration and weathering) is required and the consequences of the relatively low closure temperature for Sr diffusion in many minerals, especially biotite, must be considered.

Cross-References

- ▶ [Apatite](#)
- ▶ [Chromatography](#)
- ▶ [Feldspar](#)
- ▶ [Metamorphic Events](#)
- ▶ [Mica](#)
- ▶ [Rb-Sr, Hydrothermal Events](#)
- ▶ [Thermal Ionization Mass Spectrometry \(TIMS\)](#)
- ▶ [U–Pb Zircon](#)

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Secondary Ion Mass Spectrometry (SIMS)

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Synonyms

[Focused ion beam mass spectrometry](#); [Ion microprobe mass spectrometry](#); [Ion microscope mass spectrometry](#)

Definition

Mass Spectrometer. Instrument for causing separation of ions according to mass.

Introduction

SIMS is a technique for generating ion beams from solid targets. A focused ion beam is used to sputter (= ablate) the target mineral. The primary ion beam is typically quite energetic (10–20 keV) and composed of chemically reactive species (O, Cs) that enhance secondary ion production in electropositive elements (metals) and electronegative species (non metals). SIMS is applied through instruments such as the ion microprobe or ion microscope. For U-Pb geochronology, a negative oxygen ion beam (O^- or O_2^-) is used to generate U^+ and Pb^+ ions. Molecular species UO^+ , UO_2^+ , ThO^+ , etc., are also commonly measured. Sputtering results in complicated mass spectra that include atomic, simple molecule, and complex molecule species.

Instrumentation

In order to distinguish between the relevant Pb^+ and $U(O_n)^+$ species, large mass spectrometers are frequently used. The first mass spectrometer used for this purpose was the SHRIMP (Sensitive High-Resolution Ion Microprobe), which had a magnet turning radius of 100 cm and a total beam path length of approximately 700 cm, allowing both high mass resolution and high sensitivity (Ireland et al. 2008). SHRIMP utilized a double focusing mass analyzer incorporating magnetic and electrostatic sectors, the electrostatic sector compensating for velocity dispersion in the magnet. CAMECA instruments also produce a similarly sized instrument (IMS 1280) based on their ion microscope range, which can be used for geochronology.

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U–Pb Geochronology

Studies suggest that instrumental mass fractionation of Pb isotopes is low (~ 0.2 % per amu) allowing use of uncorrected Pb isotope ratios. Therefore, zircons older than $\sim 1,000$ billion years can be dated using directly measured $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Younger zircons have insufficient ^{207}Pb for $^{207}\text{Pb}/^{206}\text{Pb}$ dating, but a novel calibration technique allows the use of $^{206}\text{Pb}/^{238}\text{U}$ ratios for geochronology (Compston et al. 1984).

The Pb^+/U^+ ratio is fractionated from the true Pb/U ratio because of the differences in ionization yields between U and Pb. Furthermore, the Pb^+/U^+ can be quite variable in an analytical session. Based on a model of local thermodynamic equilibrium, the measured Pb^+/U^+ is found to covary with uranium-uranium oxide speciation. Pb^+/U^+ versus UO^+/U^+ is frequently used to monitor the instrumental fractionation and allow measurement of calibrated $^{206}\text{Pb}/^{238}\text{U}$ ratios to a level of 1 % reproducibility.

Mineral Analysis

The first mineral used for ion microprobe analysis was zircon (Compston et al. 1984). The beneficial characteristics of zircon are that it contains elevated concentrations of U (100–500 $\mu\text{g/g}$), but the crystal structure strongly excludes Pb. Radiogenic Pb produced by the decay of U is strongly retained in zircon during even high-grade metamorphism. Zircons can be strongly zoned with domains representing inherited material, as well as igneous and metamorphic overgrowths. Ion microprobe analysis allows in situ analyses of growth zones that can be characterized through electron imagery (cathodoluminescence) as well as optical imagery (transmitted and reflected light) to optimize petrographic context and avoid areas complicated by inclusions or fracturing (Hanchar and Hoskin 2003). Other U-bearing minerals including monazite, allanite, titanite, and apatite have been dated.

Precision of SIMS U-Pb analyses can be limited by the small amount of material analyzed. A typical analysis consumes only a few nanograms of material. For a 100-Ma-old zircon with 100 $\mu\text{g/g}$ U, only 3 fg of ^{206}Pb are included in an analysis, many orders of magnitude below detection limits of other techniques. Precision can be further limited for materials with low uranium concentrations or young minerals where radiogenic Pb in-growth is limited.

Ion microprobe analysis has been applied to zircons younger than a million years and to zircons formed at the start of the solar system, ~ 4.56 billion years ago.

Conclusion

SIMS analysis allows a reliable means of dating discrete domains in U-Th-Pb-bearing minerals that may have complex histories. In situ analysis allows retention of the petrographic context and is one of the most powerful attributes of the technique. However, because the amount of material sampled is extremely small (few nanograms), precision can be limited, especially in young minerals or those with low uranium concentrations.

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Continental Drift (Paleomagnetism)

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Definition

Paleomagnetism is the study of the Earth's ancient magnetic field through the record of remanent magnetism preserved in rocks. The directions of remanent magnetization are used to deduce the position of the Earth's magnetic pole relative to the study location at the time when this magnetization was acquired. By studying magnetizations of varying age from a single lithospheric plate, one can construct a path of apparent polar wandering (APWP) that tracks the motion of that plate relative to the geographic pole. A well-defined APWP can serve as a geochronological tool, i.e., for dating magnetizations of unknown age through a comparison of their directions with those expected from the reference APWP. Paleomagnetism can be used to date any geologic event that engenders the acquisition of remanent magnetization, including formation of igneous and sedimentary rocks, deposition of ore minerals, episodes of deformation, and other remagnetization processes.

Introduction

The development and broad acceptance of the theory of plate tectonics in the 1960s (e.g., McKenzie and Parker 1967) was the culmination of decades of scrutiny and intense debate among the Earth science community that ultimately witnessed the establishment of a mobilistic paradigm for the Earth's surface, which had first been introduced by Wegener (1912) in the form of "continental drift." Paleomagnetism was a key to this revolution, as it provided unambiguous evidence both for the "drift" of continents (Runcorn 1956) and for seafloor spreading (Hess 1962). The latter was validated by the observation of marine magnetic anomalies, which revealed symmetric, age-dependent stripes of remanent magnetization carried by seafloor that was created at mid-ocean ridges during periods of opposite geomagnetic polarity (Vine and Matthews 1963). While the concept of seafloor spreading provided a qualitative explanation for the mechanism of continental drift, identifications of marine magnetic anomalies allowed quantitative estimates of displacements between continents through geologic time, paving the way for the development of the modern theory of plate tectonics.

The geomagnetic field averaged over a sufficiently long time interval (tens to hundreds of thousands of years) is closely approximated by the field of a geocentric dipole aligned parallel to the Earth's rotation axis (McElhinny and McFadden 2000; Merrill et al. 1996). The dipolar geometry of the time-averaged field allows paleomagnetists to estimate positions of geographic poles relative to the studied locations by analyzing directions of remanent magnetization, provided that these magnetizations were acquired over a time interval that was sufficiently long to average

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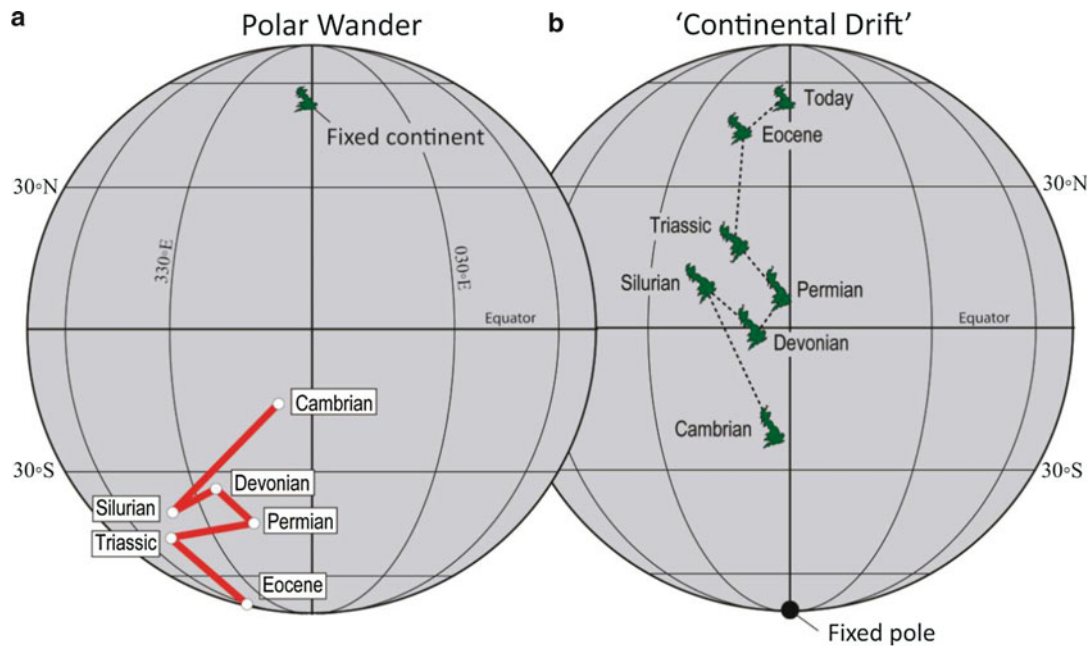


Fig. 1 (a) The first Phanerozoic polar wander path for “Europe” (Creer et al. 1954) based on six paleomagnetic poles from Britain. These poles – here shown as south poles – differ from the present-day South Pole, and this was originally interpreted as a change in the Earth’s rotation axis through time, i.e., true polar wander (TPW). In this plot, the continent (British Isles) stays fixed, but the polar axis is left to wander and following a path that is dubbed apparent polar wander path (APWP). “Apparent” means that the wandering may not be real and that it could be the result of “continental drift” as in (b). (b) The location of the British Isles at different times (longitude is arbitrary) according to the poles in (a), and here assuming a moving continent with a fixed polar axis. This was originally coined “continental drift.” Note that Scotland and England were actually separated by the Iapetus Ocean before the Silurian (Fig. 2a). This was not known in 1954 and thus the British Isles cannot be plotted as a coherent unit in the Cambrian

out short-term deviations of the geomagnetic field from that of a geocentric axial dipole (paleosecular variation). The poles obtained through measurements of magnetic remanence are commonly referred to as “paleomagnetic poles.” Due to the motion of lithospheric plates relative to the Earth’s spin axis, the position of the paleomagnetic pole in the reference frame of a specific plate varies with age. To an observer on the plate who is not aware of plate motion, it would appear that the spin axis slowly changes its orientation through time, so that the geographic pole moves along a unique path that we refer to as the “apparent polar wander path” (APWP). The motion reflected by APWPs may be due to the “drift” of individual plates, the rotation of the entire planet relative to the spin axis (true polar wander, TPW), or a combination of these two processes.

Creer et al. (1954) were the first to publish an APWP for “Europe” based on paleomagnetic poles from Britain. The paleomagnetic poles (plotted as south poles in Fig. 1a) differed markedly from the present-day pole and left Creer et al. (1954) with two possible explanations: either the pole itself had moved (TPW) or Britain/Europe (Fig. 1b) had moved relative to the pole (“continental drift”). Initially, they interpreted their results as “a slow change in the axis of rotation of the earth with respect to its surface,” in other words, TPW. However, two years later, Runcorn (1956) published an APWP for North America and crucially observed that it was separated from the APWP of Europe by $\sim 30^\circ$ longitude, thus demonstrating that the continents must have moved relative to each other. Specifically, Runcorn (1956) attributed the separation of the APWPs to the “drift” between North America and Europe corresponding to the opening of the Atlantic Ocean. This

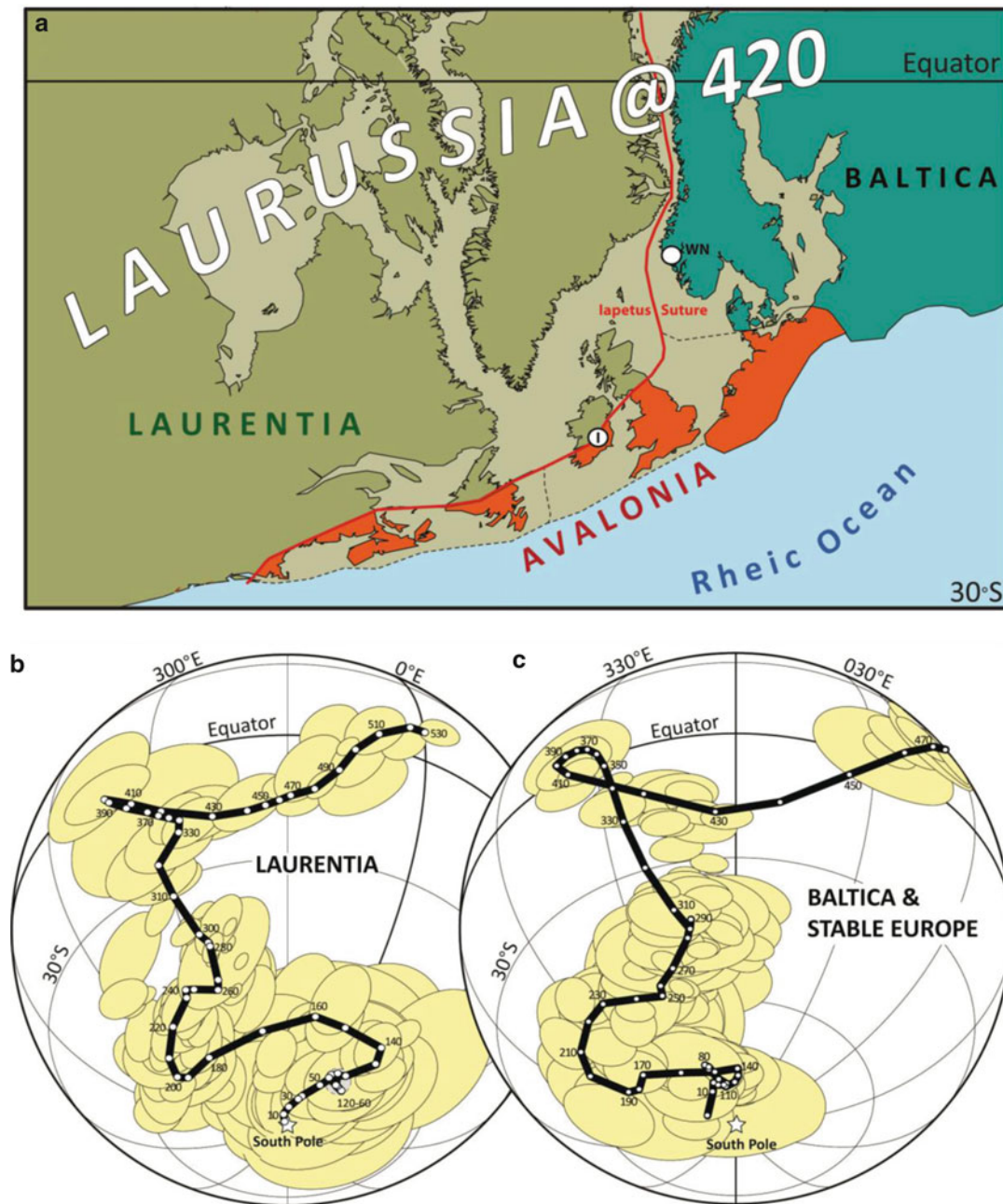


Fig. 2 (a) Reconstruction of Laurussia at 420 Ma. Avalonia collided with Baltica at ~450 Ma and later Baltica/Avalonia collided with Laurentia (including North America, Greenland, Scotland, and Northern Ireland) at 430 Ma along the Iapetus Suture. The locations of paleomagnetically dated fault rocks in Western Norway (WN) and mineral deposits in Ireland (I) are shown as *open white circles*. The Irish mineral deposits are located near the Iapetus Suture and about 50 km north of the Variscan Front in Fig. 3b. (b) APWP for Laurentia. Moderately smoothed spherical spline path shown in 10 Ma intervals from the Early Cambrian (530 Ma) to the present. (c) APWP for Baltica/Stable Europe from Early Ordovician to the present. Input poles for both Laurentia and Baltica/Europe are shown with 95 % confidence ovals (*yellow shading*) and detrital sedimentary input poles have been corrected for potential I-errors (after Torsvik et al. 2012)

interpretation was later corroborated by the analysis of marine magnetic anomalies (Vine and Matthews 1963).

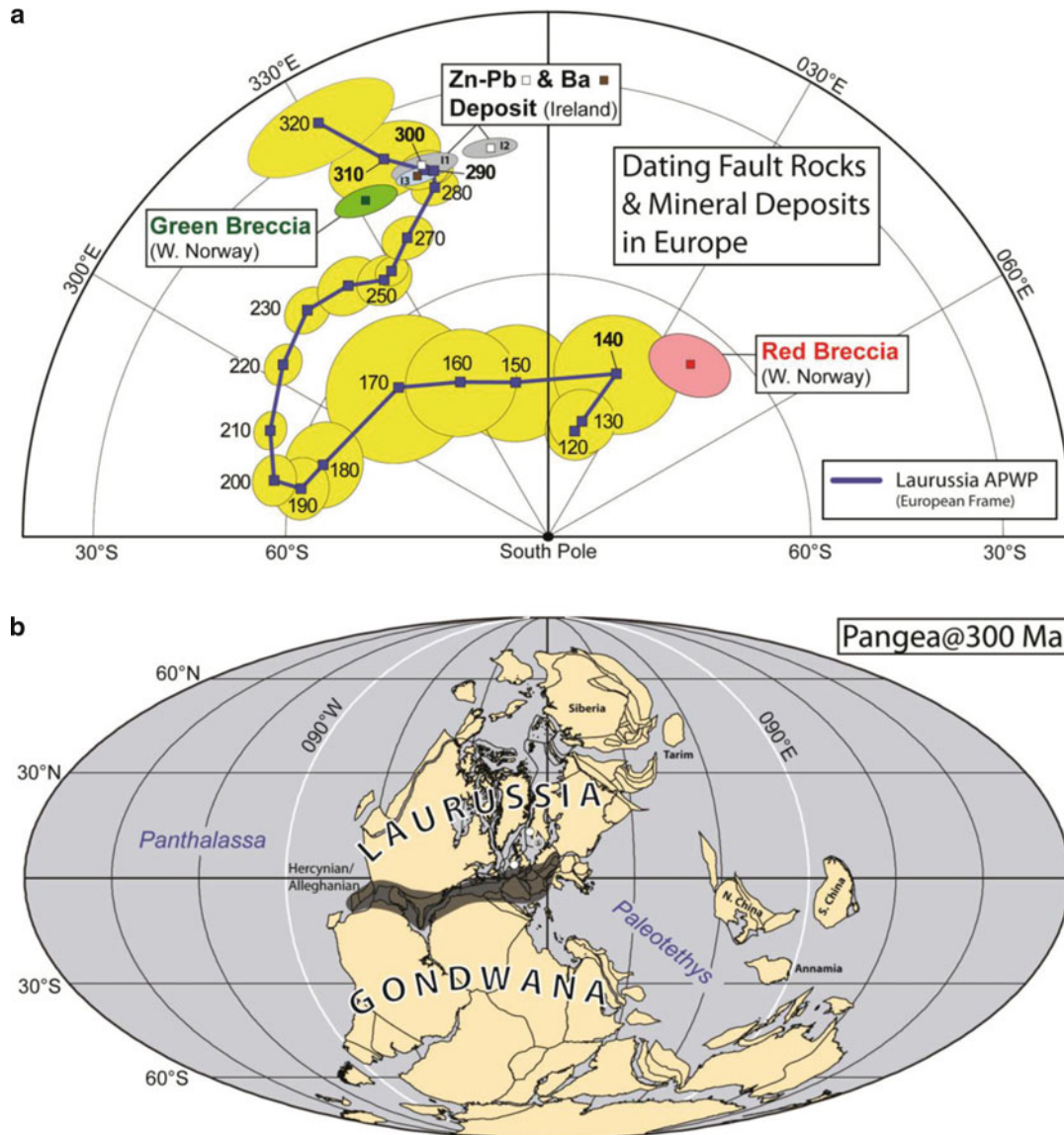


Fig. 3 (a) Laurussian (Baltica/Stable Europe and Laurentia rotated to European coordinates) running mean path shown with A_{95} circles (yellow shading). The APWP is corrected for potential inclination shallowing in detrital sedimentary rocks (Torsvik et al. 2012). The APWP is shown in 10-Myr intervals from the Late Carboniferous (320 Ma) to the Cretaceous (120 Ma), and each mean pole is based on a sliding time window of 20 Myr. The APWP is compared with paleomagnetic poles derived from two generations of fault rocks in Western Norway (Torsvik et al. 1992) and Zn–Pb and Ba deposits in Ireland (Pannalal et al. 2008a, b; Symons et al. 2007). These poles are shown with 95 % confidence ovals (dp/dm). (b) The Zn–Pb/Ba and the green breccia poles in (a) dates to around 310–290 Ma; they can potentially be linked to the waning stages of Hercynian orogenic activity

It is now well established that tectonic plates (which may include both continental and oceanic lithosphere) are constantly moving relative to each other, although at times they may coalesce or fragment, and their boundaries are otherwise frequently modified. APWPs from the individual continents attest to their often independent history of motion but also reveal an incessant, but commonly subordinate component of TPW. After more than a half-century of paleomagnetic research, the APWPs of most continents can be traced back to the dawn of the Phanerozoic, although they are generally much better defined for younger time. Consequently, when and where

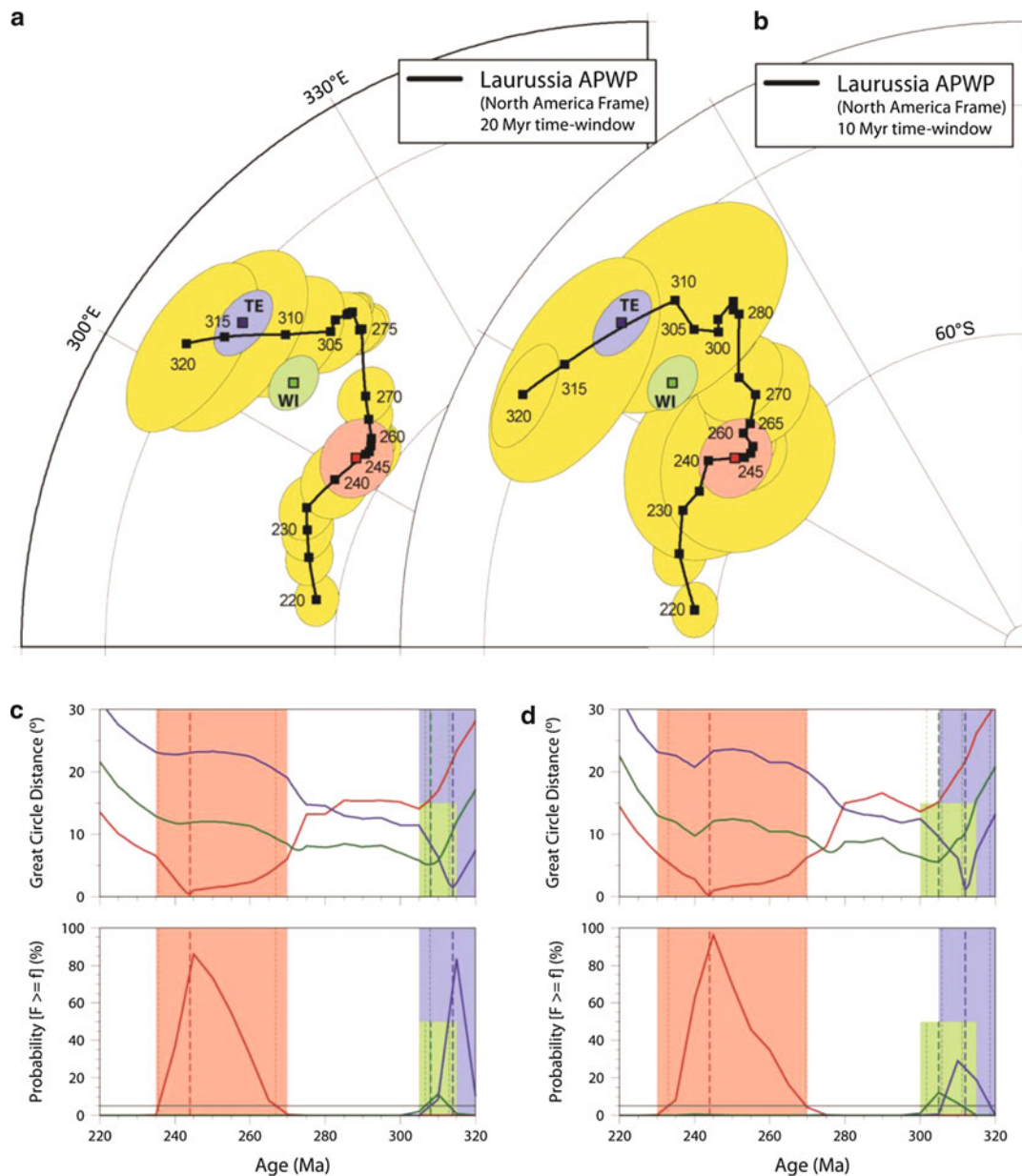


Fig. 5 (a, b) Laurussia running mean path with A_{95} circles (yellow shading) from the Late Carboniferous (320 Ma) to the Triassic (220 Ma) shown together with a paleomagnetic pole from intrusions in southern Illinois (red square with the pink A_{95} circle) from Domeier et al. (2011) and Zn–Pb mineralization poles from Tennessee (TE) and Wisconsin (WI) (black and green square with light blue and light green A_{95} circles; same as in Fig. 4, but the dp/dm ovals were recalculated into A_{95} circles using the formulations of Cox (1970)). The running mean path is shown in two versions: (a) time window = 20 Myr and (b) time window = 10 Myr. (c, d) Great circle distance and the probability of the McFadden and Lowes (1981) test for the comparisons of the poles with the APWPs ((c) 20-Myr window, (d) 10-Myr window). Red curves correspond to the pole from the southern Illinois intrusions, blue curves to the Tennessee Zn–Pb mineralization pole, and green curves to the Wisconsin Zn–Pb mineralization pole. Thick dashed vertical lines show the best estimates of ages; thin dashed lines indicate their nominal 95 % confidence limits. Shaded bands show the conservative confidence intervals (pink shading for the southern Illinois pole, light blue shading for the Tennessee pole, and light green shading for the Wisconsin pole)

these APWPs are well constrained, it is now possible to invert the traditional workflow of

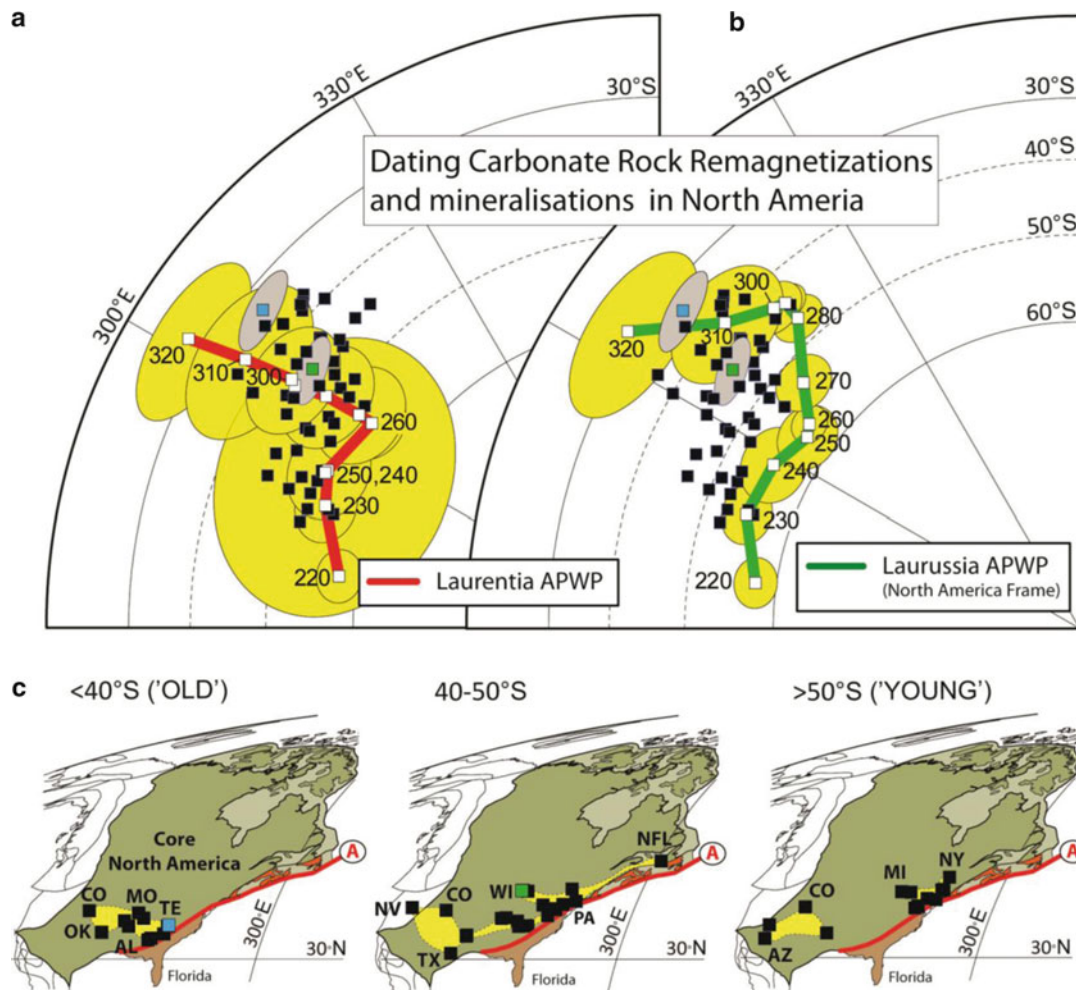


Fig. 4 (a) Laurentia running mean path with A_{95} circles (yellow shading) from the Late Carboniferous (320 Ma) to the Triassic (220 Ma) shown together with remagnetized carbonate rock poles from North America (Van der Voo and Torsvik 2012) and two Zn–Pb mineralization poles (blue squared is the pole from Eastern Tennessee, Symons and Stratakos 2002; green squared is the pole from Wisconsin, Pannalal et al. 2004). Remagnetized carbonate poles (black squares) are shown without 95 % confidence ovals for clarity. (b) Similar to (a) but the North American poles are compared with the Laurussia APWP (North American frame). (c) Geographic locations of sampling sites poles in (a–b) but plotted for sites with pole latitude $<40^{\circ}\text{S}$ (presumed oldest remagnetizations, i.e., Late Carboniferous when compared with the Laurentia APWP), $40\text{--}50^{\circ}\text{S}$ (Permian), and $>50^{\circ}\text{S}$ (Late Permian–Triassic). Yellow shading denotes regions of remagnetization and mineralization. TE Tennessee, WI Wisconsin, OK Oklahoma, MO Missouri, AL Alabama, AZ Arizona, PA Pennsylvania, MI Michigan, NY New York

paleomagnetic studies and use the APWP as a geochronological tool for dating magnetizations of unknown age.

Constructions of Reference APWPs

APWPs constructed as paths of apparent motion for the northern or southern geographic pole conveniently summarize paleomagnetic data for continents, terranes, and other tectonic blocks. In order to define an APWP, paleomagnetic poles of various ages are plotted on a stereonet and then fitted with a model path of polar motion, either with the use of spherical splines or by applying

a running mean technique. With the spherical spline method (Jupp and Kent 1987), a spline curve constrained to lie on the surface of the sphere is fitted to the paleomagnetic poles providing a regression model that smoothly approximates the positions of the poles at their respective ages (Fig. 2b–c). The paleomagnetic poles that serve as the input data for the regression are assigned statistical weights that are inversely proportional to the precision of the poles (A_{95}) or the paleomagnetic quality factor Q (Van der Voo 1990). In Fig. 2b–c, the input poles were weighted by the value of $7/Q$, which causes the spline path to pass closer to high-quality poles (7 is the highest possible value of Q factor).

In the running mean method, the position on the APWP corresponding to a specific age is calculated as a Fisherian mean (Fisher 1953) of paleomagnetic poles whose ages fall within a selected time window (e.g., 20 Ma) centered on that age. For example, the 160 Ma pole in Fig. 3a averages all Laurussian paleomagnetic poles within the 150–170 Ma age window. In practice, the mean poles are commonly calculated at age increments equal to half the width of the averaging window (e.g., 10 Ma increments for the 20 Ma window in Fig. 3a). An advantage of the running mean technique is that the pole uncertainty, commonly expressed as a circle of 95 % confidence (A_{95}), can be estimated for each mean pole through Fisherian statistics (Figs. 3–5). Both the spline method and the running mean technique effectively average out random biases of individual paleomagnetic poles and allow the basic pattern of APW to be determined.

APWPs have changed dramatically over the course of the past six decades, in part due to a much greater pool of paleomagnetic data. For example, in contrast to the initial compilation of merely five Phanerozoic poles from Britain (Fig. 1a), the most recent Phanerozoic APWP for Europe (Fig. 2c) is based on several hundred paleomagnetic poles. APWP refinements have also been made through the implementation of more sophisticated analytical methods and better instrumentation. Important recent developments include novel techniques to identify and correct for the inclination shallowing errors in data from clastic sedimentary rocks, which are now recognized to be commonly biased (Torsvik et al. 2012). An improved understanding of paleogeography has also driven notable changes in how we group paleomagnetic data. For example, the “European” path in Fig. 2c is constructed only with paleomagnetic poles from Baltica before 430 Myr, but after this time we also include poles from Scotland (originally a part of Laurentia, Fig. 2a), Avalonia (which was a separate terrane in the Ordovician), and progressively younger poles from Europe derived from rocks formed after their accretion to Laurussia. The Laurentian path in Fig. 2b is constructed from North American and Greenland poles; the latter have been rotated to North America after adjusting for the Cenozoic opening of the Labrador Sea and Baffin Bay.

The relative positions between North America, Greenland, and Baltica/Europe are known reasonably well after the Silurian, and paleomagnetic poles from these continents can be combined into a Laurussian APW path (Figs. 3 and 4b, Torsvik et al. 2012). In the following section, we will use this APWP as a reference path to illustrate the essentials of the paleomagnetic dating technique with examples of age estimates from fault rocks in Western Norway, Zn–Pb deposits in Ireland, intrusions in southern Illinois (USA), and remagnetized carbonate rocks and mineral deposits in North America.

Examples of Paleomagnetic Age Determinations

Example 1: Fault Rocks in Western Norway

After the Silurian Caledonide collision of Baltica and Laurentia (Fig. 2a), post-orogenic collapse and extensional shearing was accommodated along the Nordfjord-Sogn Detachment (NSD) in

Western Norway (e.g., Andersen et al. 1991). The NSD and Devonian mylonites are cut by younger brittle faults, most spectacularly exposed in outcrops on the island of Atløy (Torsvik et al. 1992; Eide et al. 1997) where a nearly flat-lying fault-breccia zone comprises a green network breccia crosscut by a red breccia. The magnetic mineralogy of the green breccia is dominated by magnetite, and magnetization components yielded a mean pole position that was originally assigned a Late Permian age (250–260 Ma) by Torsvik et al. (1992). The green breccia pole plots slightly off the APWP for Laurussia, but is within the 95 % confidence circle of the 310 Ma reference pole (Fig. 3a). Considering that the acquisition of fault-related remanence in the green breccia has likely occurred over a time interval that does not fully average the secular variation of the geomagnetic field (Torsvik et al. 1992), the uncertainty of the pole location may be substantially larger than that implied by its nominal 95 % confidence region (shown by a green ellipse in Fig. 3a). Hence, the post-Devonian fault rejuvenation along the NSD can only be loosely constrained to Late Carboniferous (310 Ma) to Early Permian (280 Ma) time. The red breccia pole overlaps with the 140 Ma mean pole for Laurussia (Fig. 3a), suggesting Early Cretaceous fault movements corresponding to the formation of the red breccia along the NSD.

Brittle fault rocks are notoriously difficult to date with conventional isotopic methods and $^{40}\text{Ar}/^{39}\text{Ar}$ whole-rock spectra from the breccias defined several age groups that were interpreted to correspond to separate thermal episodes (Eide et al. 1997). However, the oldest whole-rock ages from the green breccia, 296.2 ± 2.6 Myr (8 steps, 47 % of total $^{39}\text{Ar}_k$ gas) and 296.4 ± 2.8 Myr (4 steps, 58.4 % of total $^{39}\text{Ar}_k$ gas), are in agreement with the age suggested by paleomagnetic data (280–310 Ma). The youngest $^{40}\text{Ar}/^{39}\text{Ar}$ ages range from 96 ± 3 Ma to 163 ± 4 Myr and may reflect argon loss related to low-temperature hematite precipitation during the formation of the red breccia at ~ 140 Ma (Fig. 3a).

Example 2: Zn–Pb Deposits in Ireland

The Lisheen Zn–Pb deposit in Ireland is one of the major Lower Carboniferous carbonate-hosted base metal deposits, but the timing of ore mineralization and its genesis have been debated due to the lack of absolute ages. Paleomagnetic results from twelve Zn–Pb mineralized sites and eight host-rock sites (Pannalal et al. 2008a) yield a combined pole that is indistinguishable from the 300 and 290 Ma mean poles for Laurussia (pole I1 in Fig. 3a). A paleomagnetic pole (Symons et al. 2007) from the nearby Magcobar Ba deposit (pole I3 in Fig. 3a) is virtually identical to the Lisheen pole and a pole from the Galmoy Zn–Pb deposit plots slightly off the 300–290 Ma poles (pole I2 in Fig. 3a). These poles postdate peak Variscan folding and deformation (Fig. 3b), and Pannalal et al. (2008b) argued for an epigenetic model in which mineralization occurred during cooling from the Variscan thermal episode. These Irish Zn–Pb and Ba deposits were previously paleomagnetically dated through a comparison with an APWP published in Torsvik et al. (1996) that suggested a 269–290 Ma range for the age of mineralization. We now favor an Early Permian age of approximately 295 Ma based on our updated APWP (Fig. 3a).

Example 3: Remagnetization and Mineralization of Carbonate Rocks in North America

A well-documented remagnetization event is known to have widely affected Paleozoic carbonate rocks in North America. The cause of this far-reaching event remains enigmatic, but the age of the remagnetization can be deduced by a comparison against reference APWPs. This was most recently done by Van der Voo and Torsvik (2012), who also illustrated how the reference APWP for Laurentia had evolved over the past three decades. Figure 4a shows a comparison of the remagnetization poles listed by Van der Voo and Torsvik (2012, Table 1) with the most recent

APWP for Laurentia (Torsvik et al. 2012) that suggests that the remagnetization events date from the Late Carboniferous (310 Ma) to the Early Triassic (230 Ma). This range of ages is also manifested when the poles are compared with the Laurussian APWP (Fig. 4b), but the majority of the remagnetization poles plot slightly west of the main Laurussian path. This occurs because the Permian poles from Europe differ slightly from those of North America, and the inclusion of the European poles pulls the combined Laurussian APWP eastward. The reasons for this discrepancy are unclear. Because the North American and European poles of both older and younger age are in good agreement, it is unlikely that the discrepancy originates from erroneous relative fits between Laurentia and Baltica/Stable Europe. Nonetheless, this example demonstrates the importance of considering the differences among reference paths, as well as their limitations.

Remagnetization sites are located mostly within 1,000 km of the Alleghanian/Quachitan Sutures, but remagnetization has also been observed in sites as far as 3,000 km away (Fig. 4c), highlighting the broad scale of this protracted, continent-wide event. Spatial trends in the timing of remagnetization are not entirely clear (Fig. 4c), but as pointed out in earlier compilations, the southern states of Alabama, Georgia, and Tennessee near the Appalachian Suture appear to be affected earlier than those of the Central Appalachians (Miller and Kent 1988; Van der Voo and Torsvik 2012). Late Carboniferous (~310–300 Ma) remagnetization and Zn–Pb mineralization events were confined to an area from Alabama, Georgia, and Tennessee to Colorado. By contrast, Permian remagnetizations are much more widespread – from Newfoundland to Nevada – whereas Late Permian to Early Triassic remagnetizations are confined to the Central Appalachians (e.g., New York and Michigan) and the southwestern parts of North America (e.g., Colorado and Arizona). The cause of this pattern of remagnetization and its relation to the emplacement of Mississippi Valley-type deposits (e.g., Zn–Pb deposits) is still mystifying, but a commonly preferred hypothesis invokes tectonically expelled fluids driven from the Alleghanian orogenic belt (Oliver 1986).

Example 4: Intrusions in Southern Illinois (USA)

In the south end of the Illinois Basin, near the Illinois-Kentucky border (USA), a series of dikes, sills, and diatreme breccia bodies are observed to invade Devonian-Carboniferous sedimentary rocks on and around a structural dome (Hicks Dome) that is inferred to be cogenetic with the intrusive rocks. Due to extensive surface weathering and alteration, the intrusive rocks have proven difficult to classify and interpret. Consequently, many outstanding questions remain regarding their relationship to each other and to the greater tectonic framework of the region. Initial attempts to isotopically date the intrusive episode(s) ended in ambiguity, leading Reynolds et al. (1997) to employ paleomagnetism to date the rocks. From an intrusive breccia and a lamprophyric sill, Reynolds et al. (1997) isolated a remanent magnetization carried predominantly by high-temperature-oxidized titanomagnetite, as witnessed by microscopic observations of magnetite-ilmenite intergrowths that suggest a primary igneous origin of the mineral. Matching the resulting paleomagnetic pole with the APWP of Laurentia, Reynolds et al. (1997) concluded that the magnetization was acquired in late Paleozoic-early Mesozoic time during the emplacement of the intrusions. A comparison of the results of a recent paleomagnetic study that revisited these intrusive rocks (Domeier et al. 2011) with the updated APWP for Laurussia indeed reveals a close correspondence between the paleomagnetic pole and the 240–260 Ma mean poles of the APWP (Fig. 5a).

Uncertainties of Paleomagnetic Age Estimates

In the examples of the previous section, we restricted our discussion to qualitative age assignments through a visual comparison of paleomagnetic poles derived from magnetizations of unknown age with a reference APWP. In most cases, however, it is desirable to obtain a formal age estimate and specify its uncertainty. In this section, we will present a simple statistical approach that can be used to estimate the “best-fitting” age and its confidence interval.

The accuracy of ages estimated from paleomagnetic data depends on several factors, and certain conditions must be satisfied for paleomagnetic age estimates to be meaningful. It is critical that the magnetizations used to calculate a pole of unknown age have sampled a sufficiently long time interval to average out paleosecular variation (e.g., at least tens to hundreds of thousands of years) and that tectonic tilts or rotations postdating the acquisition of magnetization have been structurally corrected. When either of these two conditions is not met, the calculated pole may be significantly biased, resulting in an erroneous age estimate. In cases when it is suspected that the paleosecular variation has not been averaged out (as, e.g., in the fault breccias from Western Norway discussed in the previous section) or that there may have been unaccounted structural tilts, the most conservative approach is to conclude that whereas the pole provides some indication for a particular age, the age cannot be constrained with certainty.

Although the reference APWP can vary depending on the construction method, the differences between the spline-fitted and running mean paths that are defined using a large number of high-quality paleomagnetic poles are usually not significant (e.g., Torsvik et al. 2012). It is most common to construct running mean APWPs at 10-Myr intervals with a sliding time window of 20 Myr (e.g., Figs. 3 and 4). Irrespective of whether the reference APWP is a spline or a running mean path, the best estimate of the unknown age of the pole is the age corresponding to a position on the APWP, for which the great circle distance (GCD) between the pole and APWP is minimal. Because the reference APWPs are usually tabulated at rather large age increments (10 Ma in most cases), we recommend resampling the reference APWP at smaller steps (e.g., 1 Ma) by interpolation between the consecutive poles assuming a constant rate of polar motion, calculating GCDs between the pole and APWP at these increments, and defining the age corresponding to the minimum GCD value.

The confidence region for the estimated age can be defined by testing whether the dated pole is statistically distinct from the reference APWP at a specified level of significance (e.g., 5 % to constrain a 95 % confidence interval). In spline models, the uncertainty of the APWP is not known, and it is not possible to rigorously define the confidence region. If the spline curve intersects the 95 % confidence circle (A_{95}) of the pole, the range of ages corresponding to the APWP segment within the circle may serve as a “minimal” confidence region. Without incorporating the uncertainty of the APWP, it clearly underestimates the interval of acceptable ages.

In the running mean APWPs, the uncertainty of a mean pole (A_{95}) depends on the directional dispersion (Fisher precision parameter K) and the number (N) of the individual poles within the averaging window that have been used to define the mean. The directional dispersion reflects both the random deviations of the individual poles from the “true” mean and the differences of their ages from the mean pole age. If the ages of individual poles are evenly distributed within the averaging window (which is normally the case), the mean age is expected to be nearly identical to the median age of the window. Hence, in our simplified approach, we will not consider the age uncertainties of the mean poles separately and will treat each pole of a running mean APWP as an “unbiased estimate” of the pole corresponding exactly to the nominal age (median age of the averaging window).

The range of acceptable ages can be defined by comparing the pole of unknown age and the reference poles from the APWP and deciding whether the differences are significant at the 95 % confidence level. First-order conclusions can be made through a visual comparison of confidence regions. If the A_{95} circles of two poles do not overlap, it can be concluded that the poles are distinct at the 95 % confidence level. When one of the poles is within the A_{95} circle of the other, the difference between them is not significant. In the remaining cases, when the confidence regions overlap, but neither of the two poles is within the A_{95} of the other, the significance of the observed difference can be assessed through a formal test for a common mean (McFadden and Lowes 1981).

Suppose that the pole of unknown age was estimated from a dataset comprising N_1 individual measurements (VGPs) that yielded a resultant vector $\mathbf{R}_1$ (sum of unit vectors corresponding to the individual VGPs) and the reference pole is based on averaging N_2 paleomagnetic poles, with a resultant vector $\mathbf{R}_2$. Assuming Fisherian-distributed data, the precision parameters of the underlying distributions of VGPs and poles can be estimated as

where R_1 and R_2 are the lengths of the respective resultant vectors. In cases when the R values have not been presented in original studies (which is common for the running mean APWP compilations), they can be computed from the Fisher (1953) equation for A_{95} :

The statistics f for testing the null hypothesis that the two directional datasets (VGPs and poles averaged by the running mean) can be drawn from Fisherian distributions sharing a common mean is calculated using the equation

where R_c is the length of the resultant vector for the combined dataset ($\mathbf{R}_c = \mathbf{R}_1 + \mathbf{R}_2$). McFadden and Lowes (1981) showed that this statistic is approximately distributed as the F distribution with 2 and $2(N_1 + N_2 - 2)$ degrees of freedom, and the probability of observing the test statistic as large as f or larger is

The probability $P(F \geq f)$ corresponds to the significance level for retaining the null hypothesis. Hence, if it is smaller than 0.05, we can conclude that the poles are distinct at the 5 % significance level. Otherwise ($P \geq 0.05$), the poles should be considered indistinguishable at that level of significance.

Considering that the ages of the reference poles that are not distinguishable from the pole of unknown age at the 95 % confidence level should be within the confidence interval for the estimated age, and the ages of the reference poles that are distinct from the pole should be outside this interval, the confidence limits can be defined by the range of ages for which the probability values calculated using Eqs. (3) and (4) are equal or greater than 5 %. In practice, we recommend performing the McFadden and Lowes (1981) test for all poles of the reference APWP, plotting the calculated probability as a function of age, defining the age interval for which the probability curve is above the 5 % value, and using this interval as a nominal 95 % confidence region. A more conservative estimate can be obtained by using the ages of the two closest reference poles that significantly differ from the dated pole (i.e., fail the test) as the upper and lower confidence limits. The “conservative region” may in fact be preferable because of the simplifying assumptions for the treatment of pole uncertainties discussed above and the approximate nature of the test itself (see McFadden and Lowes 1981, for discussion).

To illustrate this technique, we will now derive formal age estimates and their confidence limits for some examples discussed in the previous section (examples 3 and 4). In Fig. 5a and b, we show

the Laurussia APWPs calculated at 5-Myr increments with two different time windows, 20 and 10 Myr. The pole from the southern Illinois intrusions (example 4) plots directly on the APWPs, and the analysis of GCD values suggests an age of 244 Ma for both comparisons (Fig. 5c and d). The probability values for the McFadden and Lowes (1981) test (Eqs. 3 and 4) are plotted as solid red curves in Fig. 5c and d, suggesting a 236–267 Ma confidence region for the age estimated using the APWP with the 20-Myr window (Fig. 5c) and a 233–270 Ma region for the estimate obtained with the 10-Myr-window APWP (Fig. 5d). The conservative estimates are 235–270 Ma and 230–270 Ma, respectively. Using similar analysis for the Tennessee and Wisconsin Zn–Pb mineralization poles (example 3) and the 20-Myr-window APWP (Fig. 5a and c), we arrive to the age estimates of 314 Ma (308–320 Ma nominal confidence interval, 305–320 Ma conservative confidence interval) and 308 Ma (307–313 Ma nominal confidence interval, 305–315 Ma conservative confidence interval), respectively. With the use of the 10-Myr-window APWP (Fig. 5d), the estimates become 312 Ma (306–319 Ma nominal confidence interval, 305–320 Ma conservative confidence interval) for the Tennessee pole and 305 Ma (302–311 Ma nominal confidence interval, 300–315 Ma conservative confidence interval) for the Wisconsin pole.

The examples considered here illustrate the sensitivity of the estimated ages and their precision to the choice of a reference APWP. In all examples, the ages estimated using the APWPs with the 20-Myr and 10-Myr averaging windows do not differ significantly (the differences are below the uncertainty limits). The reference poles in the 10-Myr-window APWP have larger uncertainties (A_{95}), producing slightly wider confidence intervals for the estimated ages. This result shows that there is no real advantage in using a reference path with an averaging window shorter than 20 Myr for obtaining a better constrained age (smaller confidence region). Hence, we recommend using APWPs constructed with a 20-Myr window for most applications of paleomagnetic dating technique.

Our examples also illustrate that the precision of paleomagnetic age estimates critically depends on the rate of polar motion (spacing of reference poles along the APWP). A 40-Myr-long confidence interval for the estimated age of the southern Illinois intrusions can be tracked back to a virtual standstill between ~245 and 265 Ma in both APWPs, whereas higher rates of polar motion over the 300–320 Ma period produce much tighter confidence intervals for the Zn–Pb mineralization poles from eastern Tennessee and Wisconsin (10–15 Ma). Thus, the temporal resolution of the reference APWP imposes a fundamental limitation on the precision of ages estimated using paleomagnetic data.

Summary and Conclusions

APWPs have proven invaluable as a means to succinctly communicate plate motions, as well as a convenient tool by which to study them. Well-defined APWPs may be used as a geochronological tool, capable of revealing the unknown age of a magnetization according to the position of the paleomagnetic pole derived from it on a reference APWP. The paleomagnetic dating method can be used to deduce the age of any geologic event which produces an attendant remanent magnetization, assuming there is a well-characterized APWP corresponding to the age and area (continent/terrane) of the event. We have presented several case studies which demonstrate the application of this method to the dating of intrusive rocks, faulting, ore mineralization, and regional remagnetization. We have also discussed a simple statistical technique that can be used to derive a best-fit estimate of the unknown age and constrain its 95 % confidence interval. It is important to note that random but persistent short-term variations in the geomagnetic field (paleosecular

variation), uncertainties of the reference APWP, and its temporal resolution (rate of polar motion) impose fundamental limitations on the geochronological resolution of this method. Even the most ideal paleomagnetic result would normally yield a paleomagnetic pole with an intrinsic uncertainty of $A_{95} \approx 5^\circ$, which would roughly correspond to an age error of approximately ± 11 Ma if the host continent had a N-S drift of 5 cm/year and its APWP was perfectly defined. A slower plate speed and/or a poorly defined APWP will see an increase in the age uncertainty. Finally, a word of caution: paleomagnetic results dated by this technique cannot subsequently be used in the construction of an APWP unless their age is verified independently, as the estimated age of the magnetization is derived from the path itself.

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Magnetometer

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Definition

An instrument used to measure the intensity and direction of the remanent magnetization of specimens.

In the middle of the last century, the astatic magnetometer was widely used in paleomagnetic laboratories for the measurement of the natural remanent magnetization (NRM). It is based on a magnet pair that is equally and oppositely magnetized, and this magnet system twists in response to the direction and intensity of magnetization of the specimen beneath it. The measurement limit of these instruments was about 10^{-3} amperes per meter (Am^{-1}), for a standard 2.5×2.1 cm cylinder (Collinson 1983).

Today, the most common instruments used for the measurement of the NRM are spinner and cryogenic magnetometer, like those manufactured by Agico, 2G Enterprises, and Cryogenic Limited, among others.

Many different spinner magnetometers have been developed, but they all involve spinning a rock specimen within or adjacent to a magnetic field sensor (typically a conductive pickup coil or fluxgate element). This rapid rotation places significant demands on the physical competence of specimens. The models available commercially can measure magnetizations less than 10^{-5} Am^{-1} (McElhinny and McFadden 2000).

Cryogenic magnetometers use a detector called a SQUID (superconducting quantum interference device) that is maintained at liquid helium temperatures and are based on the properties of a superconducting ring. This instrument has greater sensitivity and speed of measurement than spinner magnetometers and can measure magnetizations of 10^{-6} Am^{-1} .

Pass-through cryogenic magnetometers are now available that can be used to measure “U-channels” and either whole cores or split half-cores, without the necessity of physically sampling the cores.

The main disadvantage of cryogenic magnetometers is the requirement of having to keep the sensing coil superconductive, since this normally requires immersion in liquid helium.

Recently, 4.2 K cryocoolers have been used without the need of liquid helium. High-temperature SQUIDs are able to operate at liquid nitrogen temperatures, but the increased thermal noise prevents them from attaining the sensitivities available for conventional SQUIDs (Williams 2007).

A new magnetometer is now under development, the spin-exchange relaxation-free (SERF) atomic magnetometer, based on the precession of the spins of alkali atoms in the vapor phase. It is anticipated that SERF atomic magnetometers could achieve sensitivities exceeding those of SQUID devices (Shah et al. 2007).

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Isua Supracrustal Belt, West Greenland: Geochronology

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Synonyms

[Isua greenstone belt](#)

Definition

The 35-km-long by up to 4-km-wide Isua supracrustal belt (ISB) lying within the Isukasia terrane, southern West Greenland (Fig. 1), consists of ca. 3,700 and 3,800 million years old (Ma) volcanic and sedimentary rocks that are among the oldest on the Earth. The ISB is the most significant and highly studied region for understanding early Earth chemistry and environments. This is because of its great antiquity and excellent exposures of a diverse range of rock types, including pillow basalts and banded iron formations (BIF).

Introduction

The ISB belt has been recognized for more than 40 years to be a significant resource for revealing early Earth history, as it contains the most extensive and least deformed sequences of Eoarchean (>3,600 Ma) ancient rocks deposited on Earth's surface. Although all rocks >3,600 Ma have undergone some degree of heating (metamorphism) and deformation due to later tectonic events, portions of the ISB rocks contain the world's least heated and least deformed oldest rocks and therefore more faithfully record their early history and processes of formation. The ISB is dominated by meta-volcanic amphibolites of island arc tholeiite and picrite geochemical affinity, some preserving pillow structures with lesser amounts of clastic and chemical sediments including quartz-magnetite banded iron formation, metachert, dolomites, and some felsic schists and pelites of volcano-sedimentary origin. The ISB lies within a larger complex of Eoarchean rocks composed mainly of quartzo-feldspathic orthogneisses derived from granitic rocks (Fig. 1).

The term *Isua* or *Isua supracrustal belt* is sometimes generically (and incorrectly) applied to all Eoarchean (>3,600 Ma) rocks from the >3,000 km² ancient terranes of West Greenland; however, these terms should only be reserved for this specific region and the term *Itsaq gneiss complex* (*Itsaq* is the Greenlandic word for ancient) as defined in Nutman et al. (1996), used when referring to the entire assemblage of >3,600 Ma rocks in the region.

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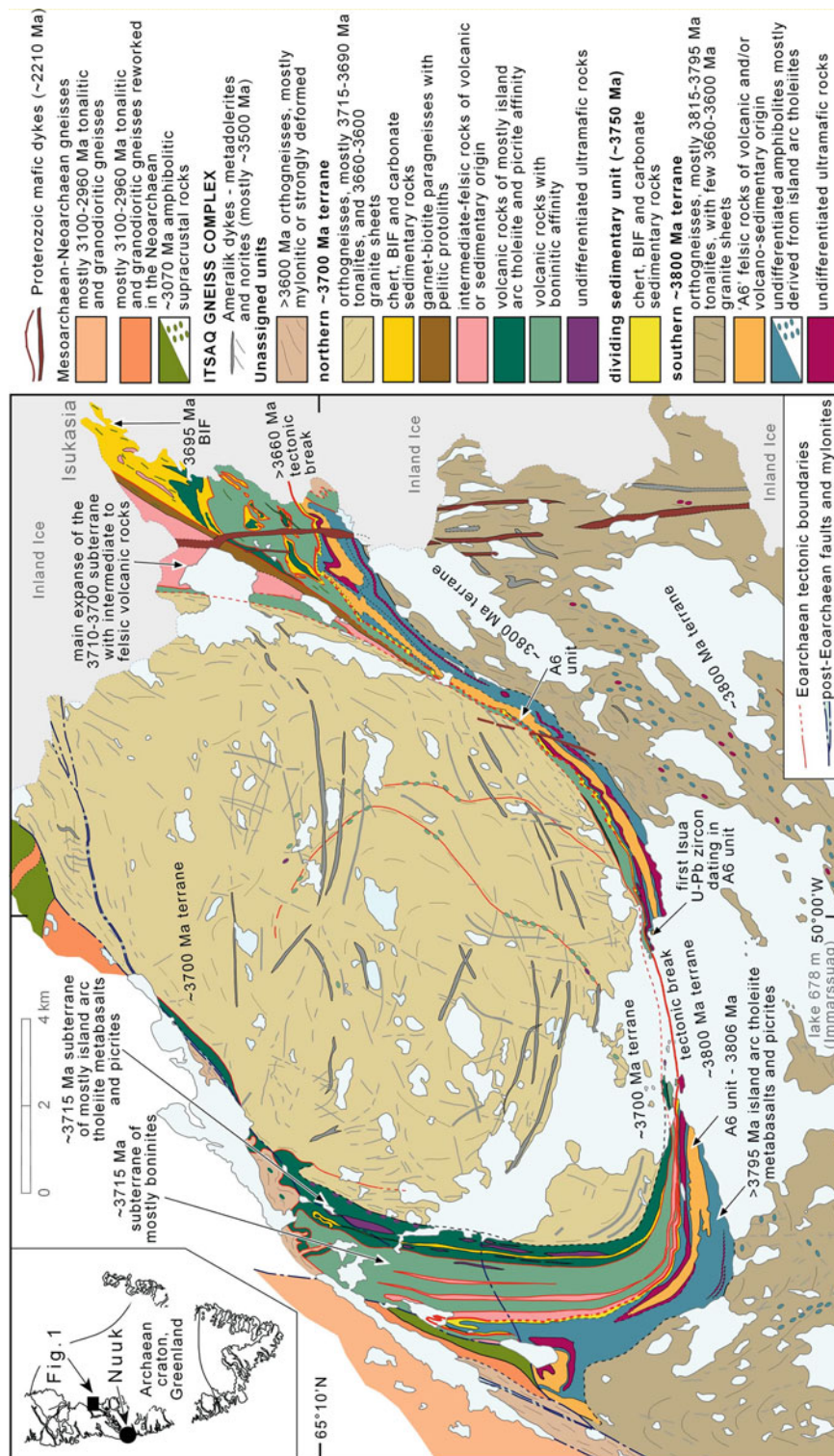


Fig. 1 Summary geological map of the Isua area, Nuuk region, West Greenland. The arcuate Isua supracrustal belt is composed of two temporally distinct terranes, both containing a range of volcanic and metasedimentary rocks. The northern terrane has rocks with ages of ca. 3,700 million years old and the southern terrane with rock ages of ca. 3,800 million years old (constrained by >30 zircon U/Pb age determinations – see Nutman and Friend 2009). The legend lists the rock types present in each terrane

History of Geochronology

The first mapping of the Isua region in 1967 was done by geologists employed by prospecting companies, with the first visit by academic geologists (S. Moorbath and V. McGregor) in 1971. Following this visit Moorbath and coworkers at Oxford University produced the first radiometric age determination (Moorbath et al. 1972; ~3,695 Ma banded iron formation indicated on Fig. 1) for the ISB using the whole rock *rubidium-strontium* isochron dating method. This early work established an age for the ISB of $\geq 3,700$ Ma, making these the oldest volcanic and sedimentary rocks then known. However, owing to the limitations of the method, this age had large uncertainties (>100 myr). Other attempts to date the age of the ISB using *Pb-Pb*, *rubidium-strontium*, and *samarium-neodymium isochrons* also confirmed the great antiquity of these rocks, but again with large uncertainties (a detailed review of the history of the investigation of the ISB is provided in Nutman and Friend 2009). *U-Pb zircon* geochronology (Baadsgaard 1976; Michard-Vitrac et al. 1977; first zircon dating site indicated on Fig. 1) also confirmed the great antiquity of the rocks, but with much improved precision. Because variations in the ages of adjacent rock units could not be resolved with this level of precision, the whole of the ISB was regarded until the mid-1990s as a single assemblage formed at more or less the same time.

A breakthrough in geochronology, particularly for determining the ages of Archean rocks arrived in mid-1980s, with the first development of in situ methods for U-Pb dating of zircon crystals using the Sensitive High Resolution Ion MicroProbe (*SHRIMP*), designed and built at the Australian National University. With this instrument 25- μm -wide sites in single zircon crystals, extracted from rocks, could be individually dated with a precision on the $^{207}\text{Pb}/^{206}\text{Pb}$ age commonly better than 10 Ma. The first SHRIMP U-Pb zircon dating at Isua (Compston et al. 1986) used the same sample as Baadsgaard and achieved a far superior pooled precision of ± 2 Myr (2σ) for the entire dated zircon population. As detailed U-Pb SHRIMP geochronology became increasingly available for ISB rocks (e.g., Nutman et al. 1997), it could be demonstrated that the ISB contained two unrelated packages of volcanic rocks differing in age by about 100 Ma. Combined with detailed mapping (available now as 1:20,000 scale maps in Nutman and Friend 2009), this showed that the ISB contains two unrelated sequences of rocks. The northern supracrustal terrane has ages of ca. 3,700 Ma and the southern terrane has ages of ca. 3,800 Ma (summarized in Fig. 1). The juxtaposition of these two separate regions occurred by 3,660 Ma, as determined by the age of the oldest unit common to both terranes.

Intensive U-Pb dating efforts by various groups using both solution single zircon crystal (e.g., Crowley 2003) and in situ large ion probe methods, with now more than 30 ages available for the ISB as compiled in Nutman and Friend (2009), have confirmed the earlier findings and extended to $>3,900$ Ma the ages of individual detrital zircon crystals within sediments. However, despite intensive searches, so far there is no U-Pb zircon evidence for $>3,900$ Ma rocks in the ISB or surrounding areas.

Current Investigations

After more than 40 years of investigation, the ISB is still the prime natural resource for the study of Earth's early history and is visited regularly by teams of researchers from institutions worldwide. Examples of past work have included using the presence of basalts with pillow structures and the identification of water-deposited chemical sediments to demonstrate the presence of liquid water on the surface of the Earth at 3,800 Ma. The geochemical characteristics of the least altered volcanic rocks in both the northern and southern ISB terranes have chemical affinities with those of younger

subduction-related rocks. This has been used to argue for the formation of ancient crust in convergent margin, plate tectonic processes on the early Earth (see review of chemistry of Isua volcanic rocks in Polat et al. 2011). Ongoing research by various groups is focused on using a range of chemical and isotopic signatures preserved in these oldest sediments and volcanic rocks to reveal the chemistry of the early ocean and atmospheres, to trace the chemical development of the continental crust and mantle reservoirs, and to search for evidence of early life.

Cross-References

- ▶ [Acasta Gneiss](#)
- ▶ [Earth's Oldest Rocks](#)
- ▶ [Rb-Sr Dating](#)
- ▶ [Sm-Nd Dating](#)
- ▶ [Uranium-Lead Zircon](#)
- ▶ [Zircon](#)

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Sediments, Terrestrial (Paleomagnetism)

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Synonyms

Magnetic polarity stratigraphy; Magnetostratigraphy

Definitions

Geomagnetic north/south poles: the points where the axis of the geocentric magnetic dipole that best fits the geomagnetic field intersects the surface of the earth. The south (north) pole of the best fitting dipole is actually in the northern (southern) hemisphere during Normal polarity, and is, by convention, called the north (south) geomagnetic pole.

Virtual geomagnetic poles (VGP's): the geomagnetic poles corresponding to the geocentric dipole that would produce an observed palaeomagnetic direction. VGP's are calculated from the declination and inclination of a paleomagnetic measurement and the latitude and longitude of the site from which the measurement was obtained.

Magnetostratigraphy: *the application of the well-known principles of stratigraphy to the observed reversal pattern of the geomagnetic polarity recorded in rock sequences.*

Paleosecular variation: *the gradual changes in direction and intensity of the geomagnetic field observed at all locations on the Earth's surface on timescales of years to millennia.*

Introduction

Paleomagnetism has become a standard discipline in dating the terrestrial record as it can be used to date and correlate sedimentary successions from all over the globe. It uses the well-documented variations in polarity, direction, and intensity of the Earth's magnetic field that have been independently dated by radiometric, astronomical, or other dating techniques. The geomagnetic polarity timescale (GPTS) is a "bar code" of alternating normal and reversed polarity intervals with characteristic lengths (Fig. 1). Sedimentary successions can be magnetostratigraphically dated by correlating their individual polarity patterns to the GPTS, with each recognized reversal providing an age tie point. The duration of individual polarity intervals varies from 20,000 years to several Myr, so that this technique will mainly work for long (>1 Myr) and continuous successions. The most recent polarity reversal (Brunhes/Matuyama) took place ~780,000 years ago. Since then several "excursions," thought to be failed or aborted reversals, have been recorded against a background of continuous low amplitude changes in direction and intensity, known as the geomagnetic secular variation. The combination of continuous records from sedimentary cores

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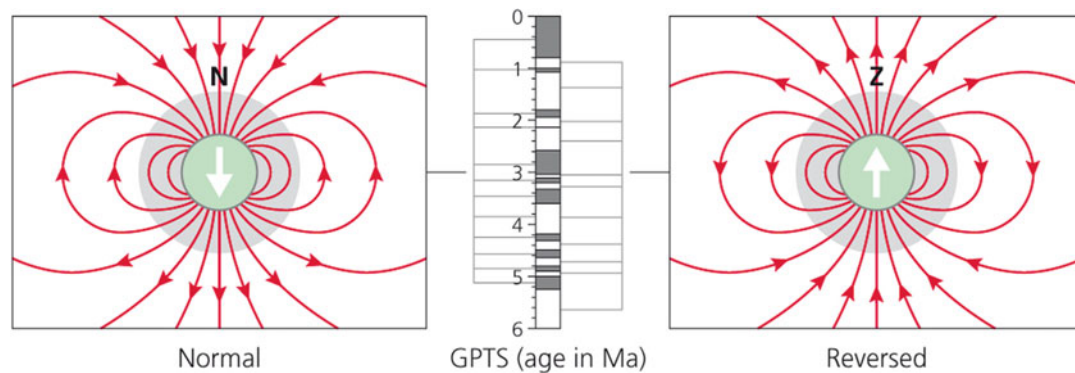


Fig. 1 Schematic representation of the geomagnetic field of a geocentric axial dipole (“bar magnet”). During normal polarity of the field, the average magnetic north pole is at the geographic north pole, and a compass points northwards. During normal polarity, the inclination is positive (*downward directed*) in the northern hemisphere and negative (*upward directed*) in the southern hemisphere. Conversely, during reversed polarity, a compass needle points to the south; the inclination is negative in the northern hemisphere and positive in the southern hemisphere. In the GPTS, periods of normal and reversed polarity are represented by *black*- and *white*-colored intervals, respectively

with data from archaeomagnetic studies has resulted in the construction of regional secular variation master curves and models. Holocene lake sediments can be dated by correlating their direction and, in some cases, their intensity records to these secular variation master curves. Terrestrial sediments are generally more difficult to date than marine sediments because the continuity of the depositional record is more easily disrupted by erosional or nondepositional processes and because biostratigraphic information (the fossil record) is often scarce.

The Paleomagnetic Signal of Terrestrial Sediments

The magnetic field at any point on the Earth’s surface is a vector that is described by three parameters: its strength (F), declination (D) – the angle, measured eastwards, between geographical north and the horizontal component of the field – and inclination (I), the angle of the field below the horizontal (Fig. 2). Ferrimagnetic grains that are deposited by wind and water experience a torque and tend to align with the ambient magnetic field as long as they are in the water column or in the soft water-saturated topmost layer of the sediment (Fig. 3). These grains will become mechanically locked by dewatering and compaction and will preserve the ambient magnetic field direction as depositional remanent magnetization (DRM). Compactional processes, however, may also affect the orientation of elongated magnetic grains and result in a shallowing of the inclination (e.g., Tauxe 2010). The paleomagnetic signal of terrestrial sediments may also be affected by secondary components of magnetization. Secondary magnetic minerals may grow chemically within the sediment, and their magnetization will become locked when they grow through a critical grain size, after which their remanence may be stable over billions of years as chemical remanent magnetization (CRM). These geochemical processes may result in the (partial) removal of the original paleomagnetic signal and in a secondary component that may be significantly younger than the deposition of the sediment. Such processes may offset the position of a reversal boundary by a time of up to tens of thousands of years. In most sediments, however, the offset is small and the paleomagnetic signal may be considered as reliable and near-depositional. Inclination shallowing does not occur in CRM because chemical growth continues after dewatering.

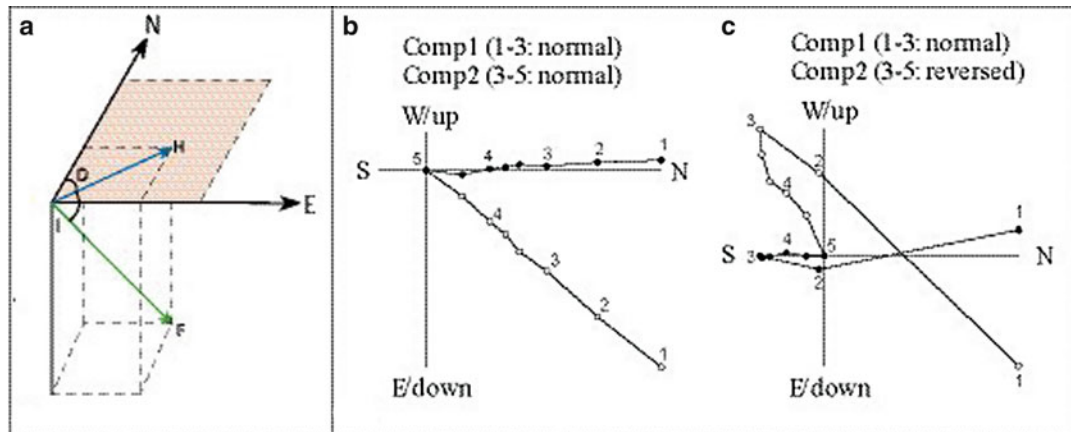


Fig. 2 (a) The magnetic field at any point on the Earth's surface is a vector (F) which possesses a component in the horizontal plane called the horizontal component (H) which makes an angle (D) with the geographical meridian. The declination (D) is an angle from north measured eastward ranging from 0° to 360° . The inclination (I) is the angle made by the magnetic vector with the horizontal. By convention, it is positive if the magnetic field vector points below the horizontal and negative if it points above. (b) and (c) The standard method for presentation and analysis of paleomagnetic demagnetization results is called the Zijderveld diagram (Zijderveld 1967). The endpoint of the vector measured after each demagnetization step is projected both onto the horizontal plane (closed symbols) and onto the vertical plane (open symbols). Difference vectors (lines between data points) then show the magnetization removed between steps



Fig. 3 Illustration of how rocks acquire a depositional remanent magnetization. When magnetic particles are eroded from a source rock and are deposited as a sediment, the particles can align with the geomagnetic field to give rise to a depositional remanent magnetization (DRM). If the sediment is remobilized (e.g., by bioturbation), high water contents can allow the magnetic particles to realign with the geomagnetic field via the torque exerted on such particles by the field (From Roberts and Turner (2013), after Tauxe and Yamazaki (2007))

In terrestrial sediments, early diagenesis is widespread and occurs in virtually every sedimentary environment. Depending on the role of organic matter, existing magnetic minerals may dissolve, iron may be mobilized, and it may precipitate elsewhere. Suitable environments for paleomagnetic dating are generally those with a sufficiently high sedimentation rate, a significant detrital input, and a predominantly oxic environment. Sediments that are deposited under oxic conditions typically contain the iron oxides magnetite (Fe_3O_4) and/or hematite ($\alpha\text{-Fe}_2\text{O}_3$) that are both magnetically stable, especially if they are fine-grained. These conditions are common in many alluvial, fluvial, and deltaic depositional environments. Sediments that are deposited under anoxic

or dysoxic conditions may contain iron sulfides like greigite (Fe_3S_4) and pyrrhotite (Fe_7S_8). Pyrrhotite is generally considered to form during late diagenesis and therefore not suitable for paleomagnetic studies. Greigite can form authigenically any time after deposition, which complicates the interpretation of its paleomagnetic records (Roberts et al. 2011). Recent studies, however, show that two particular populations of greigite may provide reliable records of the ancient geomagnetic field variations, biogenic components of primary origin generated by magnetotactic bacteria living near the sediment/water interface, and authigenic components of secondary origin that formed by early diagenetic processes (Vasiliev et al. 2008). Greigite is especially common in restricted lacustrine and brackish water (e.g., Black Sea) environments.

The paleomagnetic signal in terrestrial sediments is extremely small compared to that of volcanic rocks and lavas and strongly depends on the magnetic carriers. Magnetite-bearing sediments usually yield a much stronger paleomagnetic signal than hematite- or greigite-bearing sediments. Rocks with relatively fine grain sizes (clay, marls, silts, fine sands) usually provide the best results, because smaller magnetic particles are generally more stable.

Sampling and Laboratory Techniques for Magnetostratigraphy

Paleomagnetic samples of rocks and consolidated sedimentary outcrops are commonly collected in the field using a portable electrical or gasoline-powered drill with a water-cooled diamond drill bit. Rocks can also be drilled with compressed air, e.g., if the cooling water dissolves the unconsolidated rocks (e.g., Dupont-Nivet and Krijgsman 2012). The drilling direction (azimuth and dip) of the cores is measured (and marked) in the field by a magnetic compass and a clinometer before extraction from the outcrop. Alternatively, samples can be collected as oriented blocks which need to be drilled in the laboratory later. Standard paleomagnetic cores have a diameter of ~ 2.5 cm and are at least 2 cm long. For unlithified deposits, oriented samples are often obtained by pushing PVC sample boxes into the soft sediment and orienting them before extraction.

Ideally, the ancient geomagnetic field can be reconstructed from its record in rocks during the geological past. The primary paleomagnetic signal, i.e., originating from near the time of deposition, however, is often contaminated with chemical overprints and “viscous” remanent components, referred to as VRM. Such a VRM may result from partial realignment of “soft” magnetic domains in the present-day field or from low-temperature oxidation of magnetic minerals. Weathered rocks will most certainly yield a paleomagnetic signal overprinted in the present-day field. Overprints can generally be removed through magnetic “cleaning” by demagnetization techniques.

The standard demagnetization procedure is to progressively remove the remanence of the samples by applying stepwise increasing temperatures or alternating fields (AF) in a magnetically shielded environment. After each demagnetization step, the remaining remanence is measured on either a spinner or a cryogenic magnetometer. Most rocks contain several components of magnetization, which are demagnetized within different temperature (or AF) ranges. If these components are formed at different times, they often have recorded the paleomagnetic field with a different direction. In the ideal case, the decay of the remanence will be linear within separate demagnetization ranges, so that direction and intensity of individual components can be reliably determined. The stepwise demagnetization results are commonly displayed in so-called Zijderveld diagrams or Z-plots (Fig. 2b, c). Their advantage over stereographic projections is that they enable resolution of the relative intensity and directions of the various linear components. The direction is usually determined by principal component analysis and is documented by declination, inclination, and maximum angular deviation (MAD).

Magnetostratigraphic Dating of Terrestrial Sediments

There are several prerequisites for the successful application of magnetostratigraphy as a dating technique for terrestrial sedimentary sequences (Opdyke and Channell 1996; Langereis et al. 2010). First, the originally recorded geomagnetic field has to be retrieved with sufficient accuracy and resolution to enable the successive intervals of normal and reversed polarity to be faithfully determined. Second, one needs to have some approximate (biostratigraphic or radiometric) age control. Finally, the studied sequences must represent a sufficiently long period to reveal a characteristic pattern of polarity intervals (generally >1 Myr during the Cenozoic) that can be unambiguously correlated to the standard GPTS. Naturally, hiatuses and major changes in sedimentation rate may obscure this “barcode” pattern, requiring careful field observations, while sampling resolution must ideally be several times higher than the shortest duration of (sub)chrons (20–30 kyr). Sampling of multiple sections, covering the same stratigraphic interval, increases the reliability of the age determination.

Often, these prerequisites are met, enabling magnetostratigraphy to be used as a high-resolution age control, which has several fundamental advantages above other dating techniques (Opdyke and Channell 1996; Langereis et al. 2010). Unlike most biostratigraphic events, reversals of the geomagnetic field are globally synchronous events, within sampling resolution, allowing precise correlations between different parts of the world and between different environments. A successful correlation of the recorded polarity pattern to the GPTS provides accurate ages of every recognized reversal boundary, allowing estimation of rates and rates of change (Fig. 4). This enables, for example, detailed continental-marine correlations and hence the determination of synchrony or diachrony of regional or even global paleoclimatic or tectonic events. Magnetostratigraphy can also be used to study the paleogeographic evolution and paleoclimatic history of different regions over long periods.

The latest development in dating the terrestrial record comes from orbital tuning of observed sedimentary cycles to cyclic changes in Earth’s orbit around the Sun and its axial tilt. In the “astronomically tuned polarity timescale,” each reversal boundary – or any other geological boundary for that matter, e.g., biostratigraphic datum levels or stage and epoch boundaries – is dated individually. The astronomical polarity timescale (APTS) has provided a breakthrough in dating of the geological record (Hilgen et al. 1997) and has significantly increased our understanding of, for example, the (paleo)climate system, since astronomical tuning relies on deciphering and understanding environmental changes driven by climate change which in turn is orbitally forced. Some parts of the geological timescale – e.g., the Late Triassic and the Middle Miocene – are largely based on astronomically tuned polarity reversals documented in terrestrial sediments (Kent and Olsen 1999; Abdul Aziz et al. 2000).

Geomagnetic Excursions

There is growing evidence from dynamo theory and the paleomagnetic record that for every successful polarity reversal, there have been a number of unsuccessful attempts of the geodynamo to reverse. Theory suggests that this is due to the longer magnetic time constant of the inner core: a reversal is initiated in the liquid outer core, but the inner core often fails to reverse before the initiating anomaly has reverted to the original polarity. In the paleomagnetic record, an excursion is seen as a significant deviation of the direction of magnetization – the virtual geomagnetic pole moving more than 45° from the rotation axis and a drop in intensity to maybe 20 % or 30 % of its

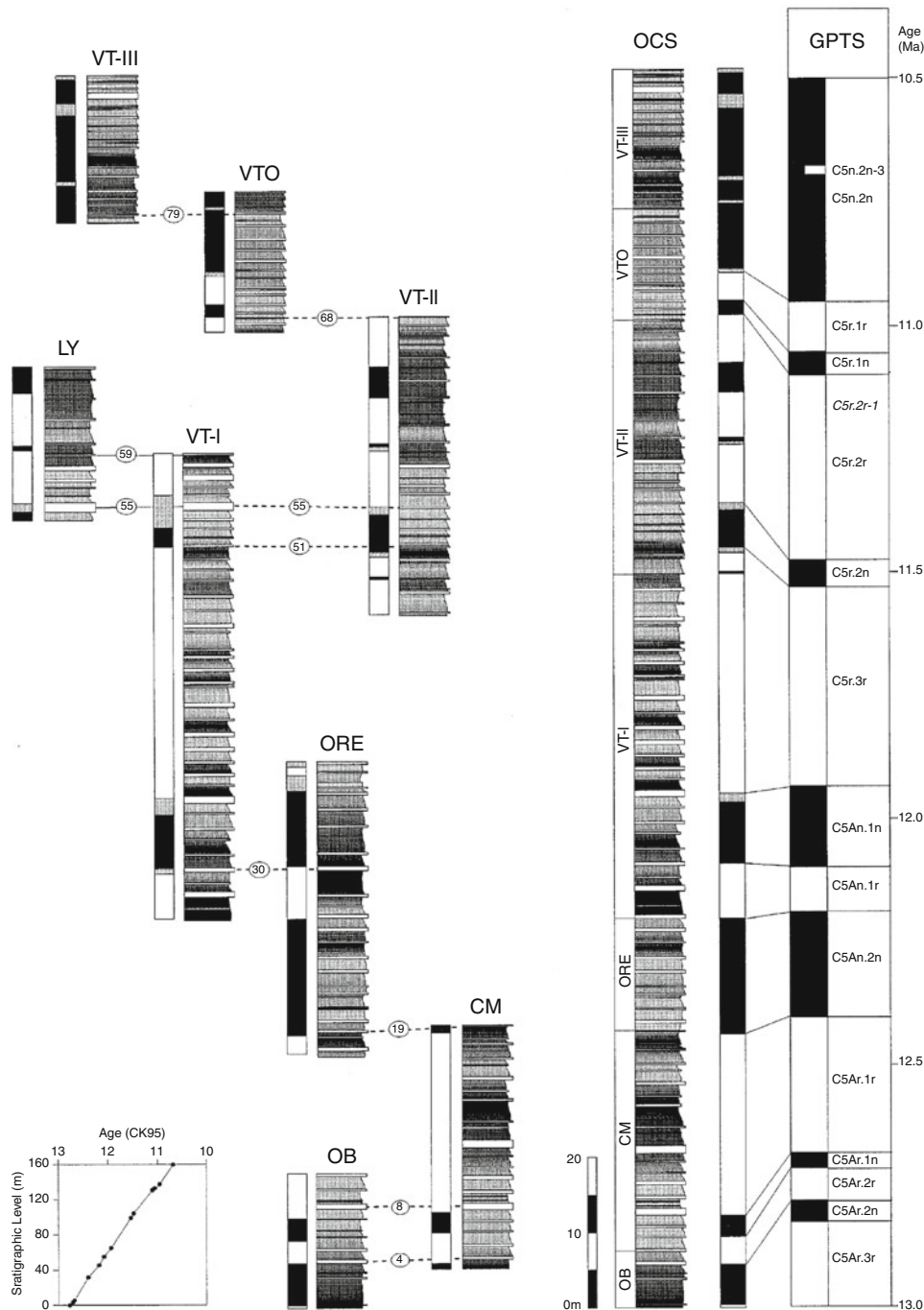


Fig. 4 Cyclostratigraphic and magnetostratigraphic correlations between subsections and correlation of the terrestrial Orera composite section (*OCS*) to the GPTS. The *OCS* is located in the continental Calatayud Basin of NE Spain. Solid lines between *OCS* and GPTS connect (interpretative) concomitant polarity boundaries. The inset diagram illustrates the changes in accumulation rates through time (After Abdul Aziz et al. (2000))

value during steady polarity. Many excursions are observed worldwide and therefore make good global stratigraphic markers. In the Brunhes these include the Mono Lake (33 ka), Laschamp (41 ka), Blake (120 ka), Iceland Basin (180 ka), Pringle Falls (210 ka), Big Lost (570 ka), and Stage 17/Delta (670 ka) (e.g., Roberts and Turner 2013).

Paleosecular Variation Curves of Holocene Lake Sediments

Secular variation refers to the gradual changes in the geomagnetic field that occur at all locations on the globe on timescales of years to millennia and are due to changes in the internal geodynamo. At any given location, the direction may vary by several tens of degrees and the intensity by a factor of two or more over a few centuries. In general the variations are not regular but consist of characteristic time-varying signals in each of the three components. Spherical harmonic analysis of historical observations made over the past 400 years shows that all the Gauss coefficients vary with time indicating that both the dipole and non-dipole field contribute to the secular variation (Jackson et al. 2000).

Several prerequisites are of crucial importance for paleosecular variation studies. Sediments should be fine-grained and contain single-domain detrital or biogenic magnetic minerals in sufficient concentration to yield a stable magnetization that can be measured with accuracy. They should have accumulated in a quiet environment, free from currents that might otherwise upset the alignment of magnetized grains as they fall, settle, and are locked into position in the sediment (Fig. 3). In many cases, the direction of such a detrital remanent magnetization (DRM) is an accurate record of the paleomagnetic field direction; however, sometimes the inclination appears to be shallowed during the depositional process, resulting in erroneously low average inclinations. Techniques are available for detecting and estimating a correction for such inclination error (e.g., Tauxe 2010).

Lake and shallow marine sediments typically accumulate at rates of between 0.5 and 5 m per millennium, and so the DRM of such sediment sequences can, in favorable circumstances, provide a continuous high-resolution record of prehistoric (or paleo-) secular variation (Tauxe 2010). The intensity of a DRM depends on the intensity of the paleomagnetic field and a complex function of the properties of the magnetic grains carrying the remanence. In order to obtain an estimate of paleointensity, a normalizing factor must be found that gives an empirical estimate of this function. In principle this should be a laboratory-grown remanence that affects the same spectrum of magnetic grains as the DRM, that is, it has a similar magnitude and coercivity spectrum. In practice normalization using anhysteritic remanent magnetization (ARM) is often found to yield a good proxy for relative paleointensity in sequences where there is little variation in magnetic mineralogy or grain size (Levi and Banerjee 1976; Tauxe and Yamazaki 2007).

Coring and Sampling for Secular Variation Studies

When coring unconsolidated subaqueous sediments for paleomagnetism, the most important considerations are to core vertically, to avoid rotation of the core barrel which might upset the declination record, and to avoid disturbance of the sediment due to compaction or vibration. Piston corers, operated from boats or small ships, are the usual choice. The Mackereth corer (Mackereth 1958), made of nonmagnetic materials, is operated pneumatically from cylinders of compressed air and collects 6, 9, or even 12 m long cores in a single drive. Once cut into 1.0 or 1.5 m sections and split into halves, cores are sampled either in discrete, typically 2.0–2.5 cm plastic cubes, or in continuous U-channels of 2 × 2 cm cross-section and up to 1.5 m in length. Many laboratories now employ pass-through cryogenic magnetometers to measure the NRM of U-channel samples continuously; some also have in-line automated alternating field demagnetization instrumentation (Turner et al. 2007). A downside of such automation, however, is that the measured signal is a convolution of the magnetization and the sampling profile of the sensors and deconvolution

should be performed (e.g., Jackson et al. 2010). Measurement of discrete samples is more time-consuming but circumvents the convolution problem. Clearly there is a trade-off between time and resolution: with very long marine cores, the efficiency of automated measurements on U-channels wins, but with Holocene secular variation records from perhaps 6 m long cores, the extra resolution often makes discrete samples preferable.

Secular variation “master curves” are now available covering the Holocene period in several parts of the world. Typically these have been compiled by correlating and combining the records of replicate cores within lakes and then combining such records from different lakes. Where lakes are more than about 100 km apart, the directional records are reduced to a common location, usually via a virtual geomagnetic pole transformation (e.g., Roberts and Turner 2013). Age control is typically provided by radiocarbon dating, pollen assemblages, tephra identification, etc. The stacking of several records also allows the estimation of statistical confidence in the records. An example is the UK master curve of declination and inclination of Turner and Thompson (1981, 1982) and later European records in which many of the same features are recognizable, modified increasingly with distance from the United Kingdom.

Confidence in such lake sediment records is enhanced by their correlation with archaeomagnetic records from the same region (Fig. 5). Archaeomagnetic data derived from the thermoremanent magnetization (TRM) imparted to an artifact (pottery, brick, fireplace, cooking stone, etc.) the last time it cooled through the Curie temperature of its constituent magnetic minerals. Age control may be available directly from the historical context or may be provided by radiocarbon dating of associated organic material. Although archaeomagnetic records lack the continuity of sedimentary ones, the TRM process leads to a stronger remanence. Further, there is little or no smoothing or averaging in either the magnetization or measurement process, so confidence in the direction is usually very good, and in addition an estimate of absolute paleointensity can often be made from a TRM.

Databases, Models, and Dating Tools

Various compilations of lake sediment and archaeomagnetic secular variation data are available, many in online databases. Most of these have been compiled with the aim of producing mathematical models of the geomagnetic field, and the datasets included all fulfill agreed quality criteria. The overall distribution of available data is heavily biased towards the northern and Atlantic hemispheres, and relatively few archaeomagnetic data are older than 3 ka.

Various models have been constructed using these data. The CALS suite of models (e.g., Korte et al. 2011) are continuous time-varying models of the global field based on spherical harmonic expansion of the magnetic potential in space and cubic B-splines in time. The most recent of these, CALS10k, covers the entire Holocene to degree and order 10. As is to be expected, such models are most reliable where the data coverage is best, for example, Europe and North America. In such regions, they are useful dating tools: a model master curve can be calculated for any given location (latitude and longitude) and observed declination, inclination, and/or intensity matched, either by eye or using formal statistical procedures. In other regions, where data are currently sparse, the reliability of global models and their potential for dating is poorer and will improve as more data accumulate.

An alternative approach is to model the high-density data at the regional level: to produce regional models, using only a restricted dataset. Whereas spherical harmonic analysis is a well-validated technique for use in a spherical reference frame such as the Earth, methods for producing

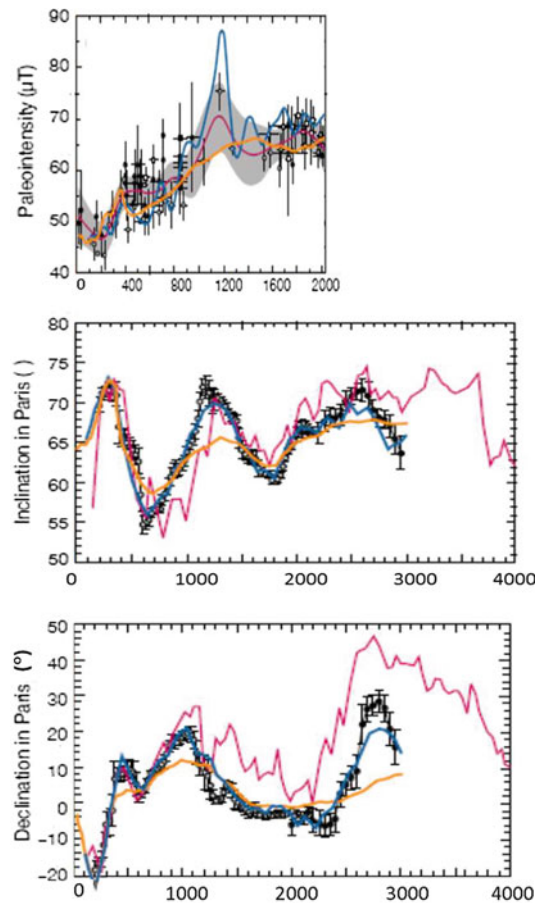


Fig. 5 Paleomagnetic secular variation records from Europe for the past 4,000 years. Declination and inclination: *black data points* with error bars are archaeomagnetic data averaged over 160-year windows, calculated at 50-year intervals, with 95 % confidence intervals, from Bucur (1994) and Gallet et al. (2002). *Red curves* are the UK lake sediment records of Turner and Thompson (1981, 1982), transformed to the latitude and longitude of Paris. Paleointensity: archaeomagnetic intensities from Spain, France, Norway, and Denmark, referred to the latitude of Paris from Gómez-Paccard et al. (2008). The *red curve* and *shading* represent the mean and 95 % confidence. In all three plots, the *blue* and *yellow curves* are calculated from the regional and global models, SCHA3k and CALS3k of Pavón-Carrasco et al. (2009) and Korte et al. (2009), respectively (After Roberts and Turner (2013))

models on restricted areas of the globe are less well developed. One method is spherical cap harmonic analysis (Haines 1985; Thébaud et al. 2006), which has been used to produce models for Europe, SCHA.DIF.3k and SCHA.DIF.8k (Pavón-Carrasco et al. 2010). Although the method is still controversial, these European models reproduce the data as well as or better than existing global models based on spherical harmonic analysis (Fig. 6).

Pavon-Carassco et al. (2011) have gone one step further – they have produced a Matlab dating tool, whereby input of a paleomagnetic declination, inclination, and ideally intensity, together with sampling location, results in an estimate of age, based on comparison with a PSV master curve for the location that is calculated from regional and global models. The next decade will almost certainly see both improvements in global models and the appearance of PSV-based dating tools for many more regions of the globe.

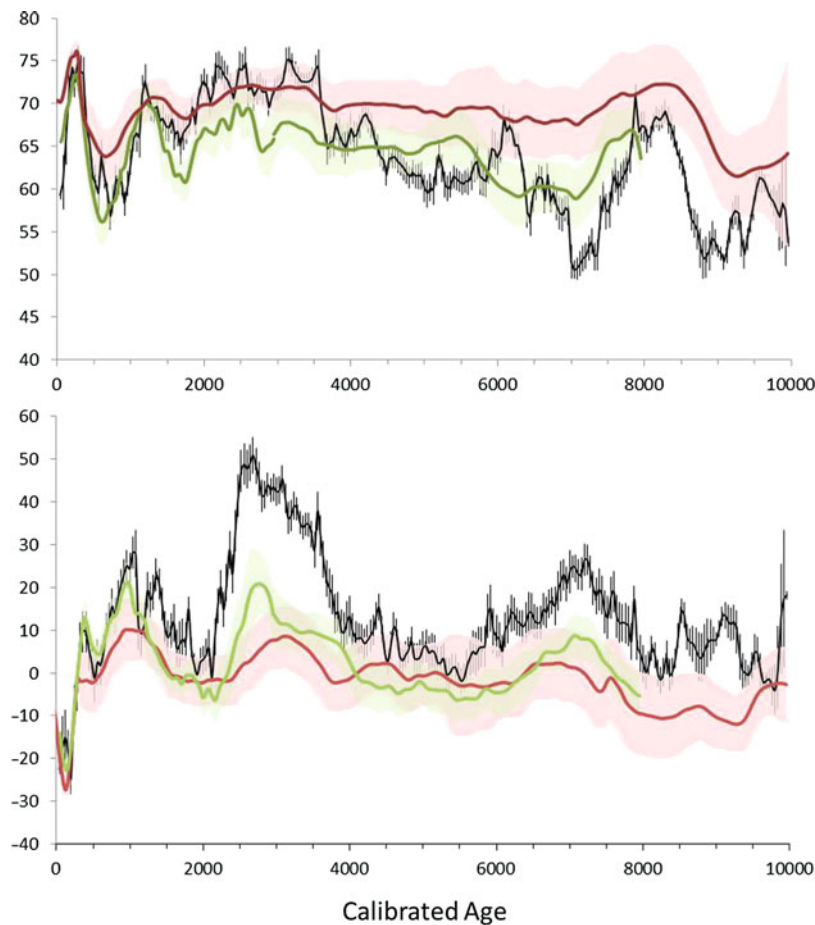


Fig. 6 *Black*: Paleomagnetic secular variation “master curve” for the United Kingdom, compiled from ten 6 m long sediment core records (four from Loch Lomond, three from Windermere, three from Llyn Geirionydd) with age control provided by suites of radiocarbon dates on three of the cores (From Turner and Thompson (1981, 1982)). *Red*: Modeled declination and inclination variations at the latitude and longitude of Loch Lomond calculated from the CALS10k model, which is based on spherical harmonic analysis of globally distributed secular variation records (Korte et al. 2011). *Green*: Modeled declination and inclination variations at the location of Loch Lomond calculated from the SCHA3k and SCHA8k models, which are based on spherical cap harmonic analysis of European secular variation records (Pavón-Carrasco et al. 2009, 2010). In each case, the uncertainty bars and bands signify 95 % confidence limits

Summary/Outlook

Paleomagnetic records of polarity reversals and secular variation can provide valuable age control for geological and archaeological materials, particularly sedimentary sequences. The geomagnetic polarity timescale is applicable worldwide. Secular variation is coherent over regions of continental scale. The use of regional master curves of declination, inclination, and sometimes intensity is gradually being supplanted by mathematical models at regional and global scale from which dating tools can be created. The current GPTS offers high-resolution age control for the past 160 Ma, where it is constructed from seafloor magnetic anomaly profiles, complemented by astronomical and radiometric ($^{40}\text{Ar}/^{39}\text{Ar}$; U-Pb) dating of terrestrial rocks. Research is now focused on excursions and older parts of the GPTS. Secular variation models will be improved as more data is obtained to fill in the gaps, particularly in the southern hemisphere and Pacific regions.

Cross-References

- [Archaeomagnetic Dating](#)
- [Continental Drift \(Paleomagnetism\)](#)
- [Geological Time Scale](#)
- [Geomagnetism](#)
- [Magnetic Anomalies](#)
- [Magnetic Chronology](#)
- [Magnetism, Rock and Mineral](#)
- [Magnetostatigraphic Dating](#)
- [Milankovitch Cycles](#)
- [Paleomagnetic Poles](#)
- [Sediments, Marine \(Paleomagnetism\)](#)

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Meteorites (U–Pb)

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Synonyms

$^{207}\text{Pb}/^{206}\text{Pb}$ dating; Pb-isotopic dating; Pb-Pb dating; U-Pb dating of meteorites

Definition

Determination of ages of meteorites and their components using decay of radioactive isotopes ^{238}U and ^{235}U and accumulation of their decay products (daughter isotopes) ^{206}Pb and ^{207}Pb .

Introduction

Meteorites contain trace amounts of uranium, and their ages can be calculated from the quantities of accumulated radiogenic isotopes of Pb. Two long-lived isotopes of uranium ^{235}U (0.7205 %, half-life 4.468×10^9 year) and ^{238}U (99.2736 %, half-life 0.704×10^9 year; isotopic abundances based on the data of Brennecka and Wadhwa 2012, half-lives from Jaffey et al. 1971) decay to stable isotopes of lead ^{207}Pb and ^{206}Pb . The dual nature of the U–Pb decay scheme has two important implications for geochronology (Ludwig 1998; Amelin 2006; Schoene 2014). First, consistency of the dates calculated from two parent-daughter pairs, ^{238}U – $^{206}\text{Pb}^*$ and ^{235}U – $^{207}\text{Pb}^*$ (the asterisk indicates radiogenic Pb), can be checked using concordia diagrams (Wetherill 1956; Tera and Wasserburg 1972), and their consistency provides evidence that the U–Pb-isotopic system remained closed since formation of the rock. Second, the two decay schemes can be combined, and the date can be calculated from the ratio of radiogenic isotopes $^{207}\text{Pb}^*$ and $^{206}\text{Pb}^*$. The $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates are insensitive to recent migration of U or recent loss of radiogenic Pb, so it may be possible to get accurate ages even from meteorites affected by recent impacts, terrestrial weathering, and laboratory treatment that is usually necessary for removal of non-radiogenic Pb. Modern U–Pb chronology of meteorites is based on $^{207}\text{Pb}^*/^{206}\text{Pb}^*$, whereas $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{235}\text{U}$ provide supporting information.

Concentration and Distribution of Uranium in Meteorites

Modern “terrestrial” U–Pb geochronology mainly relies on dating minerals such as zircon, baddeleyite, and monazite that usually contain 10–1,000 ppm or more U and negligible quantities of non-radiogenic Pb. In contrast, minerals with U content greater than several ppm are very rare in chondrites and their components and in achondrites of asteroidal origin. Uranium concentrations in various types of meteorites are summarized in Table 1. Because of low U concentration, several milligrams of bulk meteorite, or a chondrule or CAI material, are required for a single analysis, compared to microgram or

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Table 1 Examples of uranium concentration (in parts per million) in meteorite classes, selected meteorites, and their components

Meteorite class	Meteorite group	Component or mineral	Uranium concentration, ppm, range, and (median)
<i>Bulk meteorites and their major components</i>			
Ordinary chondrites	H	Bulk meteorite	0.009–0.135 (0.022)
Ordinary chondrites	L and LL	Bulk meteorite	0.007–0.027 (0.012)
Estatite chondrites	EH	Bulk meteorite	0.006–0.008
Carbonaceous chondrites	CI, CM, CV, CR, ungrouped	Bulk meteorite and chondrules	0.012–0.491 (0.026)
Carbonaceous chondrites	CV	Bulk Ca-Al-rich refractory inclusions (CAIs)	0.041–0.192 (0.113)
Eucrites		Bulk meteorite	0.008–0.305 (0.100)
Angrites	Quenched and plutonic	Bulk meteorite	0.030–0.302 (0.128)
<i>Rare high-U minerals in meteorites of asteroidal (non-planetary) origin</i>			
Carbonaceous chondrites	CV	Perovskite in CAIs	3–23
Chondrites and achondrites		Zircon	30–133
Angrites	Plutonic	Silica-rich apatite	11–22

Data from Kaltenbach et al. (2012) and Amelin et al. (2009) and references therein

smaller quantities of zircon and other U-rich minerals commonly analyzed in “terrestrial” U–Pb geochronology. Some meteorites contain very rare minerals with 10 ppm or more of uranium: perovskite in some CAIs in CV chondrites, silica-rich apatite in plutonic angrites, and small grains of zircon on some chondrites and eucrites. Despite the advantage provided by higher U concentrations and the evidence for usually concordant isotopic systems in these minerals, their use in meteorite U–Pb chronology has been limited because of their extreme rare occurrence. The mainstream meteorite U–Pb chronology still relies on representative fractions of whole meteorites, bulk chondrules, and CAIs and on rock-forming minerals such as pyroxene, all of which contain well below 1 ppm of uranium.

From Isotopic Ratio to the Age of a Meteorite in Five Steps

Obtaining a meaningful Pb-isotopic age of a meteorite from precise Pb-isotopic measurements involves five steps (Amelin et al. 2009, including their Electronic Annex EA-1). First, the Pb-isotopic ratios are corrected for all sources of analytical biases, such as mass fractionation, interferences, and matrix effects. Second, laboratory blank is subtracted, resulting in accurate isotopic composition of the Pb that was isolated from the sample. Third, radiogenic $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio is calculated or inferred from blank-corrected isotopic ratios that may include initial Pb, radiogenic Pb, and terrestrial contaminant Pb using an isochron (preferably) or a model date approach. Fourth, the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio is converted to a date – a measure of time, using known values of uranium decay constants and isotopic composition. Finally, the meaning of the date as marking the timing of a real, natural event is established, and the nature of this event is identified. Systematic uncertainties possibly leading to inaccuracy in $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ages of meteorites can be

introduced at all five steps, and their sources have to be carefully examined. Below we discuss two of the most important sources of potential inaccuracy in meteorite ages.

Removal of Non-radiogenic Pb

Along with radiogenic Pb, meteorites contain several components of non-radiogenic Pb: initial Pb of primordial composition, Pb mobilized from the target and projectile rocks by impacts in the parent asteroid and implanted into surrounding rocks, and terrestrial Pb introduced by weathering and handling. In U-Pb dating of meteorites containing as little as 10–200 ppb of U (and similar concentrations of radiogenic ^{206}Pb), we have to work with larger samples and rely on laboratory treatments, such as multistep acid leaching, to separate radiogenic Pb from several components of non-radiogenic Pb. Modern multistep leaching schemes produce radiogenic Pb with reasonably high $^{206}\text{Pb}/^{204}\text{Pb}$ (up to several thousands in favorable cases) from most refractory inclusions and igneous meteorites and are usable even if less efficient for chondrules. However, most radiogenic Pb is lost in the earlier leaching steps along with non-radiogenic Pb, so that the final, usually the purest, leaching steps typically contain only 5–10 % of the total radiogenic Pb. This is a serious disadvantage in dating materials of limited size or quantity, such as individual chondrules, or low-U mineral phases from CAIs and achondrites. Furthermore, acid leaching can fractionate radiogenic Pb from its parent U, thus rendering a concordance test of closed system behavior invalid. A search for alternative treatments, such as nonacidic selective dissolution of minerals and volatility-driven separation of Pb components by evaporation under controlled conditions, can bring about more efficient methods for extraction of radiogenic Pb from meteorites.

Isotopic Composition of Uranium

The $^{238}\text{U}/^{235}\text{U}$ ratio was considered constant and equal to 137.88 until recently, but several studies published since 2010 show that it is variable. Uranium isotopic variations among the CAIs, ranging from 137.409 ± 0.039 to 137.885 ± 0.009 (Brennecka et al. 2010), are most prominent. Most recent data from bulk chondrites and achondrites suggest uniform $^{238}\text{U}/^{235}\text{U}$ ratio (Bouvier et al. 2011; Brennecka and Wadhwa 2012; Connelly et al. 2012), but it is unclear whether variations at a smaller scale observed in these and ongoing studies are significant and whether the meteorite and terrestrial U isotopic compositions are significantly offset from each other. Considering possible variability, the U isotope ratios should be determined for every meteorite that is being precisely dated with the $^{207}\text{Pb}/^{206}\text{Pb}$ method. These determinations are, however, performed at the limit of analytical sensitivity of modern multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) and typically require several times larger quantities of material than Pb-isotopic analyses by ionization in thermal ionization mass spectrometry (TIMS). Development of a more sensitive method for precise (0.01 % or better) measurement of the $^{238}\text{U}/^{235}\text{U}$ ratios is one of the most desperately needed analytical advancements in U–Pb dating of meteorites. As the analytical uncertainties of U–Pb dating decrease, methods of non-radiogenic Pb removal improve, understanding of chemical and isotopic systematics of meteorite progresses, and correction for variable $^{238}\text{U}/^{235}\text{U}$ becomes one of the dominant components in the total uncertainty of meteorite U–Pb dates. Reducing this uncertainty will require thorough understanding of U isotopic variation in meteorites, along with improvements in analytical sensitivity and precision.

Precision of Pb-Isotopic Dates of Meteorites

Fast decay of ^{235}U and its high relative abundance at the time of the solar system formation make the change of radiogenic $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ over time strongly nonlinear and initially very rapid, so that the relative uncertainty of the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ dates for the oldest minerals and rocks ($>4,500$ Ma) is 3.2 times smaller than the relative uncertainty of the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio. Together with the modern advancements in techniques of isotopic analysis, this makes the $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio an exceptionally precise chronometer for ancient rocks and minerals. Precision of 0.2–0.5 Ma is now common in dating early meteoritic solids such as refractory inclusions, chondrules, and differentiated asteroidal materials (Amelin 2008; Wadhwa et al. 2009; Connelly et al. 2012). This precision is similar to that obtained with the popular extinct radionuclide systems ^{182}Hf – ^{182}W and ^{53}Mn – ^{53}Cr . In the most favorable cases, the uncertainty of the $^{207}\text{Pb}/^{206}\text{Pb}$ can be as low as 0.1 Ma, rivaling precision of the state-of-the-art ^{26}Al – ^{26}Mg dating. Similar precision levels form a strong basis for building a coherent timescale of the early solar system processes with a combination of Pb-isotopic and extinct radionuclide chronometers.

The Prospect of Further Improvement of Precision in Pb-Isotopic Dating of Meteorites

Even the most precise Pb-isotopic dates reported so far have 30–100 times larger uncertainties than the ultimate precision level based on counting statistics and the number of atoms of ^{207}Pb and ^{206}Pb consumed during analysis: about 0.11 Ma for 1 pg of radiogenic Pb and a mere 3,400 years for 1 ng of radiogenic Pb. The main sources of additional analytical uncertainties are incomplete conversion of Pb atoms in the sample to the ions that reach the detectors and noise and distortions in the ion beam registration. The efficiency of Pb ionization in TIMS using the best existing emitters is about 5–10 %, and this alone increases the counting statistics-related uncertainty by 3–4.5 times compared to the hypothetical 100 % ionization and extraction. In MC-ICPMS, another technique commonly used in meteorite U–Pb chronology, the ionization efficiency for Pb, is close to 100 %, but the limited ion extraction efficiency makes the total ion yield of even the most sensitive instrument configurations (2–3.5 %) lower than in TIMS. The detector systems also add substantial uncertainties to the isotope ratio measurements. The noise of the Faraday cup arrays with amplifiers in the current mode, which is used in modern commercial mass spectrometers, is limited by the thermal noise of the feedback resistors. This source of noise can be greatly reduced by using amplifiers with high input impedance in charge mode. Ion counting with an array of multipliers is an alternative solution for measuring very low ion beams, but it also requires many improvements in linearity, cross-calibration, gain stability, and other parameters.

Summary

The $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ form of the U–Pb method is the only extant radionuclide dating method with sufficient precision for resolving individual events in accretion of the solar protoplanetary disk and for cross-calibration with extinct radionuclide chronometers. It allows dating refractory inclusions, chondrules, and achondrites with precision of 0.1–0.5 Ma using samples of several milligrams to tens of milligrams. Accuracy of the dates is similar, if we do not consider uncertainty in the decay constants of uranium isotopes, which is only relevant in comparisons to other long-lived

radionuclide chronometers. Multistep isotope leaching can efficiently separate radiogenic Pb. Pb isotope dating must be accompanied by measurements of U isotopic ratios because of their known variability. Further substantial improvement of precision and reduction in sample sizes is likely to be achieved in the future by improvements of analytical sensitivity and reduction of all components of instrument noise and laboratory contamination.

Cross-References

- ▶ [Extinct Radionuclide Dating](#)
- ▶ [Geochronology](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Meteorites \(Lu–Hf\)](#)
- ▶ [Meteorites \(Rb–Sr\)](#)
- ▶ [Meteorites \(Re–Os\)](#)
- ▶ [Meteorites \(Sm–Nd\)](#)
- ▶ [Uranium–Lead Dating](#)
- ▶ [Uranium–Lead, Extraterrestrial, Early Solar System](#)
- ▶ [Uranium–Lead, Extraterrestrial, Planetary Materials](#)

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Ujaraaluk Unit (Nuvvuagittuq greenstone belt)

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The Ujaraaluk unit is the dominant lithological unit in the Nuvvuagittuq greenstone belt (formerly called Porpoise Cove greenstone belt) in Northeastern Canada. It is interpreted to be as old as 4.39 Ga, which would make it the oldest vestige of crust preserved on Earth (O'Neil et al. 2008, 2012). The Ujaraaluk unit is an amphibolite composed of variable proportions of cummingtonite – plagioclase – biotite $\pm$ quartz $\pm$ garnet $\pm$ anthophyllite (O'Neil et al. 2011). The abundance of cummingtonite gives the Ujaraaluk unit an unusual light beige color compared to most other dark green to black hornblende-dominated greenstone belts in the Northeastern Superior Province. The Ujaraaluk unit was formerly named “Faux-amphibolite” due to this unusual aspect (O'Neil et al. 2007).

The Ujaraaluk is mafic in composition ranging from basaltic to basaltic andesite. It is divided into three distinct geochemical groups following a chemostratigraphy within the Nuvvuagittuq greenstone belt (O'Neil et al. 2011). The Ujaraaluk at the base of the sequence is characterized by high Ti content and exhibits tholeiitic affinities with relatively flat incompatible trace element profiles. The top of the sequence consists of rocks with lower Ti concentrations. This low-Ti group is further subdivided in two subgroups with distinct rare earth element profiles. The Ujaraaluk directly above the high-Ti group displays U-shaped rare earth element profiles similar to modern boninites, whereas the rocks at the very top of the sequence are enriched in light rare earth elements and follow calc-alkaline differentiation trends. The Ujaraaluk unit also includes ultramafic bodies that can be divided into the same three geochemical groups. The ultramafic rocks are interpreted to be co-genetic olivine and orthopyroxene cumulates that fractionated from the mafic Ujaraaluk unit.

The age of the Ujaraaluk unit has been debated. Thin intrusive trondhjemitic bands are dated by U-Pb in zircon at $\sim$ 3.8 Ga (e.g., Cates and Mojzsis 2007; David et al. 2009) and provide a minimum age for the Ujaraaluk unit. Cates et al. (2013) proposed a maximum age of 3.78 Ga based on the oldest $^{207}\text{Pb}/^{206}\text{Pb}$ age on zircon from a fuchsitic quartz-rich horizon they interpreted as a detrital sediment. Darling et al. (2013) however suggested that these fuchsitic quartzites represent metasomatically altered intrusive felsic orthogneiss. Rocks from the Ujaraaluk unit and co-genetic ultramafic cumulates are characterized by $\sim$ 26 ppm variation in $^{142}\text{Nd}/^{144}\text{Nd}$ ratios that correlate with Sm/Nd ratios, with a significant number of samples displaying deficits in ^{142}Nd compared to terrestrial standard (O'Neil et al. 2012). Because of the short half-life of ^{146}Sm (68 Myr; Kinoshita et al. 2012), deviations in $^{142}\text{Nd}/^{144}\text{Nd}$ from the terrestrial standard can only have occurred while ^{146}Sm was still extant, i.e., before 4.1 Ga. O'Neil et al. (2008, 2012) interpreted the $^{142}\text{Nd}/^{144}\text{Nd}$ vs. Sm/Nd correlation to be an isochron and evidence that the rocks formed at $\sim$ 4.39 Ga. Massive gabbro sills intruding the Ujaraaluk unit yielded a ^{147}Sm - ^{143}Nd isochron age of $4,115 \pm 100$ Ma, consistent with an Hadean age for the Ujaraaluk unit (O'Neil et al. 2012).

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Cross-References

- [Age of the Earth](#)
- [Extinct Radionuclide Dating](#)
- [Geochronology](#)

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Chromatography

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Synonyms

Method for chemical separation

Definition

Chromatography is a general term describing chemical procedures for the separation of mixtures of elements or compounds. Chromatographic methods are used for both preparation and analysis of samples. A fundamental principle of chromatography is that components of a mixture will have different *distribution* or *partition* compound between a *mobile* and *stationary* phase. Distribution coefficients are a measure of a compound “preference” for either the mobile or the stationary phase. A solution containing compounds to be separated is usually dissolved in the mobile phase, which then is allowed to flow through a stationary phase. The dissolved components *elute* at different times in this flow system, the times being determined by the distribution coefficients – those that are preferentially retained by the stationary phase appear later in the *chromatogram*, which is the graphical output of the chromatographic separation.

Preparative chromatography is part of the purification of a sample prior to more advanced instrumental analysis. Many early advances in chromatography involved the extraction and separation of natural pigments found on biological samples and sediments. Examples of preparative chromatographic techniques used on geochronology include the separation of individual compounds (amino acids, lignins, chlorophyll) for radiocarbon analysis (Hatte et al. 2008; Marom et al. 2012) and separation of elements from solute mixtures for isotope ratio geochronology (Sanna et al. 2010; Isnard et al. 2012; Souders et al. 2012; Rotenberg et al. 2012). Analytical methods that follow these preparative steps often involve high-resolution, sensitive instrumental analytical chromatographic methods.

Analytical chromatographic procedures in geochronology include high-performance liquid chromatography (HPLC), gas chromatography (GC), size-exclusion chromatography, and various combinations of liquid or gas chromatography with instrumental mass spectrometric analysis. HPLC methods involve a liquid containing the mixture to be analyzed flowing under high pressure through a small diameter column containing the stationary phase. A range of HPLC methods exist, each tailored to the specific analysis to be conducted. Some involve ion-exchange chromatography (IEC), where the stationary phase is charged and interacts with solute ions as they flow through the column. Adjusting the pH of the solute during the analytical run will change the affinity of the solutes for the stationary phase. IEC is a common tool in amino acid racemization geochronology. Other forms of HPLC rely upon different polarities of the stationary and mobile phases, reverse

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phase chromatography (RPC – where the mobile phase is more polar than the stationary phase) now being a common procedure for analysis of amino acid enantiomers (D/L values) (Kaufman and Manley 1998; Penkman et al. 2013). GC methods involve a gas as the mobile phase and a thin liquid coating on a narrow-bore capillary column as the stationary phase. The mixture to be analyzed is vaporized in the injection port of a gas chromatograph, being carried through the liquid column by a carrier gas. Elution order is determined by the affinity of compounds for the solid phase. Flow rate and overall elution times are influenced by carrier gas pressure and column temperature. GC methods have also been traditional in amino acid racemization geochronology (Wehmiller and Miller 2000; Wehmiller 2013). Size-exclusion chromatography is a preparative chromatographic method useful for separation of compounds based on their molecular weight, an important step in the further analysis of individual compounds or mixtures found in geological samples. Mass spectrometric analyses often are focused on isotope ratio determinations (often with geochronological applications) and many examples exist where gas- or liquid-chromatographic systems are coupled with mass spectrometric systems to separate complex mixtures prior to the final mass spectrometric analysis.

Cross-References

- ▶ [Amino Acid Racemization Dating](#)
- ▶ [Radiocarbon Dating](#)
- ▶ [Rubidium-Strontium Dating](#)
- ▶ [Uranium Series Dating](#)

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3, 4, and 10](http://ocw.mit.edu/resources/res-5-0001-digital-lab-techniques-manual-spring-2007/videos/#3,4,and10)
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Amino Acid Racemization, Fluvial and Lacustrine Sediments (AAR)

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Synonyms

[Climate history](#); [Fossils](#); [Geochronology](#); [Lakes](#); [Rivers](#)

Definition

Amino acid racemization. The phenomenon of conversion of “left-handed” (L or “levo”) amino acids to their “right-handed” (D or “dextro”) form. In most living systems, 100 % of the amino acids are of the L form, and the conversion results in an equal mixture of D and L when the racemization reaction is complete.

Fluvial sediments, lacustrine sediments. Sedimentary material that accumulates and is preserved in river, stream, or lake environments. These can include sediments dominated by biological material (shells) and those dominated by inorganic material that may form by cementation or evaporation, such as carbonates or evaporates and mud or clay. Sediments range in age (time since deposition) from days to millions of years and are found in a variety of terrestrial sedimentary environments.

Introduction

Amino acid racemization (AAR) studies of fluvial and lacustrine deposits usually require the analysis of a biogenic mineral (e.g., bivalve, gastropod, ostracode, or egg shell) or organic material associated with these environments. These terrestrial deposits include river terrace and delta sediments, glacial and pluvial lake sediments, and eolian sediments derived from combined glacial and fluvial sources. In some cases fluvial deposits merge with coastal deposits in areas influenced by sea level change, providing an opportunity to link global ice volume (sea level) history with local fluvial stratigraphy. Archaeological studies that include AAR often involve samples associated with one or more of these terrestrial depositional processes (Johnson and Miller 1997). In many situations the geochronological study of these environments provides an opportunity for comparison of multiple dating methods (Oches et al. 1996; Owen et al. 2007; Bright et al. 2010). Additionally, when suitably calibrated, AAR results yield insights into local or regional temperature histories for the late Pleistocene (Goodfriend and Mitterer 1993; Miller et al. 1997). Examples of AAR applications in each of these depositional systems are reviewed in the following sections.

Shallow (<2 m) ground temperatures can vary significantly because of exposure and moisture conditions (Wehmiller et al. 2000). Consequently, the interpretation of AAR data from many

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fluvial, eolian, colluvial, or archaeological deposits must account for possible differences in burial temperature histories. This issue is particularly important for any sample that has experienced a large portion of its history either exposed at the land surface, heated by fire, or buried just a few cm below land surface. Lacustrine and marine samples are less vulnerable to this effect because their initial burial environment is usually under water. Many AAR studies demonstrate the effect of shallow burial heating (Wehmiller 1977; Goodfriend 1987; Miller and Brigham-Grette 1989; Ellis et al. 1996; Wehmiller et al. 2000; Owen et al. 2007), and many others indicate the potential thermal effects on relative age interpretations (Miller and Brigham-Grette 1989; Johnson and Miller 1997; Miller et al. 1997).

Fluvial and Lacustrine Deposits, Western United States

During Pleistocene glacial intervals, a series of large lakes existed in the Western United States where present-day precipitation is quite low (Reheis et al. 2012 and references therein). The modern remnants of these large lakes include Great Salt Lake (Utah), and Pyramid and Walker Lakes (Nevada). The hydrologic balance of these lake regions was vastly different from the present, involving a major increase in the ratio of precipitation to evaporation during glacial times. AAR is one of the many chronological tools applied to the development of a regional chronology for lake level fluctuation during the Quaternary, using either deposits created in the deeper portions of the lake (Oviatt et al. 1999) or shoreline deposits created around the high stand lake margins (McCoy 1987).

Lake Bonneville is the name given to the large lake that occupied what now is most of the state of Utah. AAR analyses of gastropods from various shallow-water deposits of Lake Bonneville identified five aminozones, each representing different phases of deposition during the middle and late Pleistocene (McCoy 1987; Oviatt et al. 1987). Numerical ages of these deposits are estimated using associated radiocarbon (C14) and U-Th data and volcanic ash deposits that are found in association with the oldest aminozone. Available geochronological data suggest that Lake Bonneville reached peak volumes at the end of marine isotope stages 4 and 2, roughly 60 and 12 ka, respectively (Kaufman et al. 2001), as well as at earlier times that are less well constrained. The ages of the shallow-water deposits constrain the times of maximum lake levels (deepest lake); samples from cores from near the center of the Bonneville Basin provide information on the transitional phases when lake levels may have been at low or intermediate levels (Oviatt et al. 1999; Kaufman 2003a). AAR results from these cores, also combined with volcanic ash chronology, demonstrate a long and discontinuous record of lacustrine deposition over the last ~700 ka.

Paleoclimatologic Information from Calibrated Lake Bonneville AAR Data

AAR data can be used to infer effective temperatures if the analyzed samples have been independently dated (see section “[Cross-Reference](#)” list). AAR analyses of well-dated ostracodes from late Pleistocene sediments in the Lake Bonneville record imply that full glacial (MIS 2) temperatures in the basin were approximately 10 °C colder than present (Kaufman 2003b). Effective temperatures for older units were not as cold (Kaufman 2003b). Ostracode AAR results from Summer Lake, a smaller pluvial lake in Oregon, imply unrealistically cold effective temperatures when compared with the Bonneville results, suggesting that other factors besides temperature may influence AAR kinetics in this sample type (Bright and Kaufman 2011; Reichert et al. 2011).

Western North America River Systems

The Pleistocene history of the Colorado River includes phases when large lakes were created upstream of large lava dams (see Kaufman et al. 2002). Deposits created by these large lakes are quite rare, and the ages of some potential lacustrine deposits in the Grand Canyon have been debated. AAR and ^{14}C results from mollusks and ostracodes indicate that lacustrine deposits found in the eastern Grand Canyon were formed <45 ka BP in small travertine-dammed ponds rather than in the large deep lakes that would have been formed in association with the much older (>100 ka to ~ 2 Ma) lava-dammed lakes (Kaufman et al. 2002).

At the downstream end of the Colorado River, the river's delta has changed dramatically during the past century in response to upstream water diversions. Part of this change has been documented using ^{14}C -calibrated AAR results for mollusks from beach ridges within the delta system. Nearly all the analyzed shells formed prior to 1930 and since ~ 1000 AD, indicating a decline in benthic productivity in the delta region corresponding to the time of diversion of water flow in the river (Kowalewski et al. 2000).

Fluvial terraces of the Chama/Rio Grande River system in the Espanola Basin of northern New Mexico record the downcutting of the rivers during the middle and late Pleistocene (Dethier and McCoy 1993). AAR data from gastropods found in slack-water deposits preserved on these terraces identify five aminozones with increasing D/L values found at increasing elevations above the modern river. Rapid deposition of shells and limited surface exposure are inferred, thereby minimizing shallow thermal effects on the results. The oldest of these zones is ~ 620 ka based on volcanic ash chronology (ash of the same age is used for calibration of aminostratigraphy in the Lake Bonneville sequence – see above), younger ones being estimated to represent ~ 310 , 170, 95, and <19 ka, respectively (Dethier and McCoy 1993).

Bright et al. (2010) used AAR data, along with associated ^{14}C and IRSL results, to revise the chronology of a bison-bearing fluvial deposit in northern Mexico. Previous $\text{Ar}^{40}/\text{Ar}^{39}$ ages on associated lava flows suggested an age of 440 ± 130 ka for this deposit, far older than expected for the presence of Bison in this region. The revised interpretation of the combined geochronological data indicates a late Pleistocene (<40 ka) age.

Fluvial and Lacustrine Deposits, Eastern United States and Southeastern Canada

AAR data from this region are helpful in understanding the geochronology of deposits formed during advances or retreats of the Laurentide Ice Sheet, a major influence on the climate and environment of eastern North America during the Quaternary. Ostracodes, gastropods, and bivalves are intermittently preserved in some of the classic stratigraphic sections from this region, ranging from the Mississippi River Valley to the St. Lawrence Valley. AAR data for gastropods from a broad range of sites, mostly in loess, from the Mississippi River Valley (Clark et al. 1989; Miller et al. 1993; Oches et al. 1996) define at least four phases of eolian (loess) deposition over the past ~ 750 ka, the most recent phase corresponding to the late Pleistocene Wisconsinan (MIS 4-3-2) glacial advance into the region. Elsewhere, portions of this regional aminostratigraphic record are preserved at isolated sites both within the Laurentide Ice Sheet margin (Karrow et al. 1997; Karrow 2004) and near the ice sheet margin in southeastern Indiana (Miller et al. 1993) and in the St. Lawrence River Valley (Occhietti et al. 1996). See “► [Amino Acid Racemization, Loess and](#)

[Glacial Sediments \(AAR\)](#)” for more discussion of Mississippi River Valley and also Eurasian Loess-AAR studies.

Fluvial, Lacustrine, and Glacial Deposits, United Kingdom

An extensive and detailed record of glacial, fluvial, and lacustrine sedimentation in the British Isles has provided an opportunity for many geochronological studies involving AAR analysis of nonmarine (and some marine) samples (Bowen et al. [1989](#); Bowen [2000](#); Penkman et al. [2013](#)). Many samples have been collected from interglacial stratotypes with associated faunal, floral, or archaeological information, including many with independent chronological data. The AAR studies of UK sites likely represent the most intense coverage of AAR data of any region of the world, as numerous investigations (most within an area $3^{\circ} \times 3^{\circ}$), involving many laboratories and collections have occurred over nearly 40 years. The advent of sensitive instrumentation and new strategies to isolate and analyze the most robust amino acid component now provides a regional aminostratigraphic framework for the British Quaternary record, a complex of glacial, non-glacial, fluvial, and marine sequences (Penkman et al. [2011](#), [2013](#)). Because of the relatively low effective temperatures for the region and the slow racemization rate during glacial intervals, the difference in D/L values for samples from one interglacial and the next can be small, but when these results are considered within lithostratigraphic or fluvial terrace relative age sequences, meaningful age estimates and correlations with the global marine isotopic record can be established (Penkman et al. [2011](#), [2013](#)). Aminozones corresponding to interglacial stages 11, 9, 7, and 5 are evident (Bowen [2000](#); Penkman et al. [2011](#), [2013](#)). Aminozones representing corresponding phases of deposition are recognized in the coastal-marine records of the southern North Sea (Meijer and Cleveringa [2009](#)).

The Nile River Delta

Sediments of the eastern Nile River Delta (Egypt) contain late Holocene marine bivalves and gastropods for which radiocarbon-calibrated AAR results have been obtained (Goodfriend and Stanley [1996](#), [1999](#)). As with other studies, the relative ease and inexpensive cost of AAR analyses allow for large numbers of analyses to be conducted, far more than could be done using radiocarbon alone. Calibrated AAR kinetics indicate the extent of mixing of older Holocene samples into younger deposits (Goodfriend and Stanley [1996](#)) and also indicate that this portion of the Nile Delta underwent rapid strand-plain accumulation in the ninth century A.D., likely leading to relocation of major port cities (Goodfriend and Stanley [1999](#)).

Fluvial and Travertine Deposits, Iberian Peninsula

In Central Spain, tufa deposits are found within fluvial terraces in small tributaries of the Tagus River, a region of karst terrain. AAR data for ostracodes from these terrace deposits, combined with racemization kinetic modeling for the region (Ortiz et al. [2004](#)), suggest phases of tufa deposition that correspond with most interglacial warm phases since ~400 ka (Torres et al. [2005](#); Ortiz et al. [2009](#)).

Lake Eyre Australia: Lacustrine Chronology and Paleoclimatology

As with the combined stratigraphic and paleoclimatic studies of the pluvial lakes of the Western United States, a similar record occurs in the Madigan Gulf region of Lake Eyre, South Australia, a region influenced by monsoonal precipitation (Magee et al. 1995). This playa lake has been episodically flooded during the late Quaternary, and a combination of radiocarbon, uranium-series, luminescence, and racemization data indicates that the lake reached a maximum depth of ~25 m during the early part of MIS 5. A Holocene high lake interval did not reach this same depth, and intervening phases of variable moisture and deflation during dry lakes dominated the regional history.

AAR studies of ostrich eggshell (OES) from the Lake Eyre region yield insights into the magnitude of cooling during the late Pleistocene (Miller et al. 1997). Combined ^{14}C , AAR, and luminescence data document the extent of racemization for samples with ages from last interglacial to the present, and the contrast in rates for samples <20 ka compared with those between 60 and 20 ka implies a glacial temperature reduction of approximately 8°C (Miller et al. 1997). See also the entries “► [Amino Acid Racemization, Paleoclimate](#)”; “► [Amino Acid Racemization, Egg Shell](#)”.

Summary

AAR study of terrestrial (fluvial, lacustrine, eolian, or archaeological) deposits has often been conducted in association with other dating methods that provide either calibration for AAR or insights into other processes affecting the physical record. Many AAR terrestrial studies focus on issues of correlation of local records with regional terrestrial records or global ice volume records, in order to understand the climatic links between local processes and the global record. Many of these terrestrial records demonstrate discontinuous or episodic deposition, in phase with either interglacial or glacial stages, depending on the physical process being dated. Volcanic ash or paleomagnetic geochronology establishes a calibration for the older parts of many records. Advances in instrumental technology have allowed large numbers of small samples (ostracodes, land snails, etc.) to be analyzed, thereby establishing a firm statistical basis for chronostratigraphic interpretations. The use of calibrated AAR results to infer late Pleistocene temperature histories is demonstrated by examples from the Western United States, the United Kingdom, Australia, and Jamaica.

Cross-References

- [14C Dating](#)
- [Amino Acid Racemization Dating](#)
- [Amino Acid Racemization, Egg Shell](#)
- [Amino Acid Racemization, Loess and Glacial Sediments \(AAR\)](#)
- [Amino Acid Racemization, Paleoclimate](#)
- [Cosmogenic Nuclide Dating](#)
- [Glacial Landscape \(Cosmogenic Nuclide\)](#)
- [Infrared-Stimulated Luminescence \(IRSL\)](#)
- [Lacustrine Environments \(14C\)](#)

- [Lacustrine Varves](#)
- [Luminescence Dating](#)
- [Luminescence Dating](#)
- [Luminescence Dating](#)
- [Luminescence, Fluvial Sediments](#)
- [Luminescence, Glacial Sediments](#)
- [Luminescence, Loess](#)
- [Marine Isotope Stratigraphy](#)
- [Paleomagnetism, Terrestrial Sediments](#)
- [Radiocarbon, Terrestrial Materials](#)
- [River Terraces \(Cosmogenic Nuclide\)](#)
- [Rock Surfaces \(Cosmogenic Nuclide\)](#)
- [Tephrochronology](#)

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Magnetostratigraphic Dating

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Definition

Magnetostratigraphy relies on the ability of sedimentary rocks to acquire a remanent magnetization when they form, which parallels the direction of the Earth's ambient magnetic field. Since the geomagnetic field has undergone multiple nonperiodic reversals through Earth history, a magnetic zonation of sedimentary sequences is feasible according to the polarity of the rock magnetization. A magnetostratigraphic zonation allows dividing the stratigraphic record into time slices which can be correlated worldwide. Magnetostratigraphic dating refers to the identification in the stratigraphic record of magnetozones, which can be correlated to age-equivalent geomagnetic chrons. The compiled absolute ages of geomagnetic chrons form the basis for the geomagnetic polarity time scale (GPTS), which is routinely revised with new radiometric or astronomic calibrations (Fig. 1).

Essential Concepts

The Magnetization of Sedimentary Rocks

Some minerals in nature can behave as magnets, that is, they exhibit spontaneous magnetization. They rarely represent a significant volume in sedimentary rocks, with abundances typically below detection limits of X-ray diffraction and grain size too small to be spotted by optical microscopy. Their magnetization, however, can be normally measured in the laboratory using a state-of-the-art rock magnetometer. Most common magnetic minerals in sedimentary rocks belong to the group of iron oxides and sulfides (Table 1).

The magnetization of an assemblage of magnetic particles (M) decays with geologic time (t) according to the following equation:

$$M(t) = M_0 e^{(-t/\tau)}, \quad (1)$$

where M_0 is the initial magnetization and τ (relaxation time) is the time elapsed to decay to $1/e$ of the initial magnetization. Following the Néel theory, relaxation time is defined as

$$\tau = \frac{1}{C} e^{[Kv]/[kT]}, \quad (2)$$

where C is a frequency constant ($\sim 10^{10} \text{ s}^{-1}$) and K is the magnetic anisotropy factor (Tauxe 1998). From this equation, it is derived that relaxation time is dependent on particle size (volume, v) and the thermal energy (kT). In the case of equidimensional pure magnetite with size range of $0.1\text{--}0.08 \text{ }\mu\text{m}$, relaxation time is greater than the age of the Earth, but it sharply decreases to seconds for particle sizes lower than $0.06 \text{ }\mu\text{m}$. On the other hand, magnetite particles larger than $1 \text{ }\mu\text{m}$ gradually reduce

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Table 1 Common magnetic minerals of application in paleomagnetism. *Ms* Saturation magnetization, *T_c* Curie temperature, *H_c_{max}* maximum coercivity (Evans and Heller 2003; Lowrie 1990; Tauxe 1998)

Mineral	Formula	Ms(kA/m)	<i>T_c</i> (°C)	<i>H_c_{max}</i> (T)
Magnetite	Fe ₃ O ₄	480	580	0.3
Hematite	α-Fe ₂ O ₃	~2.5	675	>5
Maghemite	γ-Fe ₂ O ₃	380	590–675	0.3
Goethite	α-FeOOH	~2	120	>5
Pyrrhotite	Fe ₇ S ₈	~80	320	>0.1
Greigite	Fe ₃ S ₄	~125	~330	>0.1

their relaxation time as their internal magnetic ordering shifts from a stable single domain to a multi-domain state. Thus, to be useful for paleomagnetic studies, magnetic minerals must occur in the appropriate size range, so that magnetic remanence remains stable over time scales comparable to the age of the rocks.

The Natural Remanent Magnetization (NRM) of rocks typically results from the addition of different magnetic components acquired since the time of rock formation. Primary magnetic components record the polarity of the geomagnetic field at the time of rock formation and thus provide the basic information for a magnetostratigraphic zonation. Secondary magnetizations acquired in later stage during geological history have no stratigraphic relevance and need to be identified and clearly separated from primary magnetizations.

The NRM signal in sedimentary rocks comprises three main types: Detrital Remanent Magnetization (DRM), Chemical Remanent Magnetization (CRM), and Thermal Remanent Magnetization (TRM). A DRM is carried by magnetic minerals incorporated into the sedimentary rock as detrital particles, either as part of the terrigenous fraction or from biogenic sources within the water column. If the magnetic grains are sufficiently small, their magnetic moments counterbalance the gravitational torques, producing a statistical particle alignment with the ambient field. A Detrital Remanent Magnetization (DRM) is blocked as early compaction reduces porosity and prevents further mechanical rotation of magnetic particles. The lock-in depth at which a DRM is fixed varies from millimeter to meter scale and depends on both magnetic mineralogy, rock type, and the sedimentary environment. In pelagic sediments, a reasonable estimate of the lock-in depth is 10–20 cm below the sediment-water interface (Opdyke and Channell 1996). If the time elapsed between sedimentation and DRM acquisition is considered of relevance, the term post-Depositional Remanent Magnetization (pDRM) may be used. Sediment bioturbation of different kinds may influence DRM, either allowing reorientation of magnetic particles giving rise to a new delayed pDRM or causing randomization of magnetic particles and erasing a preexisting DRM. Common carriers of DRM are the iron oxides magnetite and hematite, which resist chemical alteration as they are transported along the sediment transfer system. Once a DRM is locked-in, its preservation in sediments is determined by burial conditions: reducing environments that are associated with the presence of abundant organic matter can cause the dissolution of preexisting magnetic particles. Despite the lock-in depth uncertainty, DRM is taken as a reliable recorder of the geomagnetic field at the time of rock formation for most magnetostratigraphic purposes.

A Chemical Remanent Magnetization (CRM) is acquired due to authigenic formation of magnetic minerals, with the magnetic moment being blocked when the crystal grows through a critical size. Processes leading to a CRM acquisition can occur in an early post-depositional stage, but also in later stages of the rock history. A CRM is suitable for magnetostratigraphy as long as the acquisition takes place in an early post-depositional stage. A typical CRM carrier in terrestrial environments is hematite, which occurs as very fine-grained cement filling the porosity of siliciclastic sediments

(redbeds). In marine environments, authigenic magnetite may form as a product of oxidation of iron sulfides, giving rise to a stable CRM which is relatively frequent in environments influenced by changing redox conditions. Finally, an early CRM carried by authigenic iron sulfides can occur under specific burial conditions (Vasiliev et al. 2005), but their occurrence in the geological record is rare because these minerals easily undergo later oxidation.

A Thermal Remanent Magnetization (TRM) is acquired when magnetic minerals cool below their Curie temperature (Table 1), the temperature at which magnetic minerals change from paramagnetic into ferromagnetic (s.l.) behavior. Magnetization is then free to align with the ambient field until the minerals cool through their blocking temperature, representing the temperature transition at which relaxation time sharply increases from seconds to millions of years, efficiently locking magnetic moments. The TRM is typically carried by volcanic rocks forming the ocean crust, as well as stratified lava flows. The net magnetic moment of rocks carrying a TRM is several orders of magnitude greater than sediments having a DRM. Most common carriers of TRM in igneous rocks belong to the titanomagnetite solid solution series.

A time dependence exist for unblocking temperatures such that a thermoviscous magnetization may be acquired by rocks subjected to moderate temperatures over millions of years. Occurrence of a thermoviscous remanent magnetization is not uncommon if long-term deep burial occurs after sedimentation, particularly in regions of elevated geothermal gradients. A partial to total resetting of earlier (primary) magnetizations can result from thermoviscous magnetization processes.

As shown above, common processes of rock magnetization in nature are not uniquely related to the time of rock formation. Therefore, the NRM of rocks is an aggregate of multiple components of different age, each carried by a characteristic population of magnetic particles. Identification of the different NRM components is crucial for all paleomagnetic studies, and this is achieved by means of diverse stepwise demagnetization techniques (Langereis et al. 1989). Stepwise demagnetization is based on the assumption that each component is carried by a magnetic phase which has its own thermal stability and/or coercivity spectra (Table 1). Ideally, the stability fields of magnetic components do not overlap completely, so that the direction of every component can be determined. A wide overlap between components may lead to errors in the interpretation of paleomagnetic directional data.

The Geomagnetic Polarity Time Scale

The fact that the Earth's magnetic field has undergone reversals does not rely on direct observations. When Bernard Brunhes first discovered in 1906 the existence of reversely magnetized volcanic rocks, the finding was interpreted as a self-reversal artifact related to the thermoremanence acquisition process. It was Motonori Matuyama who later observed that a stratigraphic ordering existed in the magnetic polarity of successive lava flows, such as age dependence supporting the existence of past geomagnetic reversals. The parallel development of the radioisotope dating techniques allowed the birth of a first K–Ar calibrated geomagnetic polarity time scale (GPTS) back to 4 Ma (Cox et al. 1964). This first time scale was based on pairs of radiometric ages and magnetic polarity of lava flows distributed globally, a method that could not be extended to older ages because at that time the dating error exceeded the duration of chrons. The use of biostratigraphic correlation in deep sea cores allowed the construction of composite magnetostratigraphic sequences and further extension of the time scale to older ages (Opdyke et al. 1966). But, it was the discovery of seafloor magnetic anomalies which provided the unprecedented record of datable geomagnetic reversals back to Late Jurassic (Cande and Kent 1992, 1995; Gee and Kent 2007; Heirtzler et al. 1968).

The transformation of seafloor magnetic anomaly profiles into absolute ages relies on age interpolation from a selected number of radiometric dates (Fig. 1). Cande and Kent (1992) used

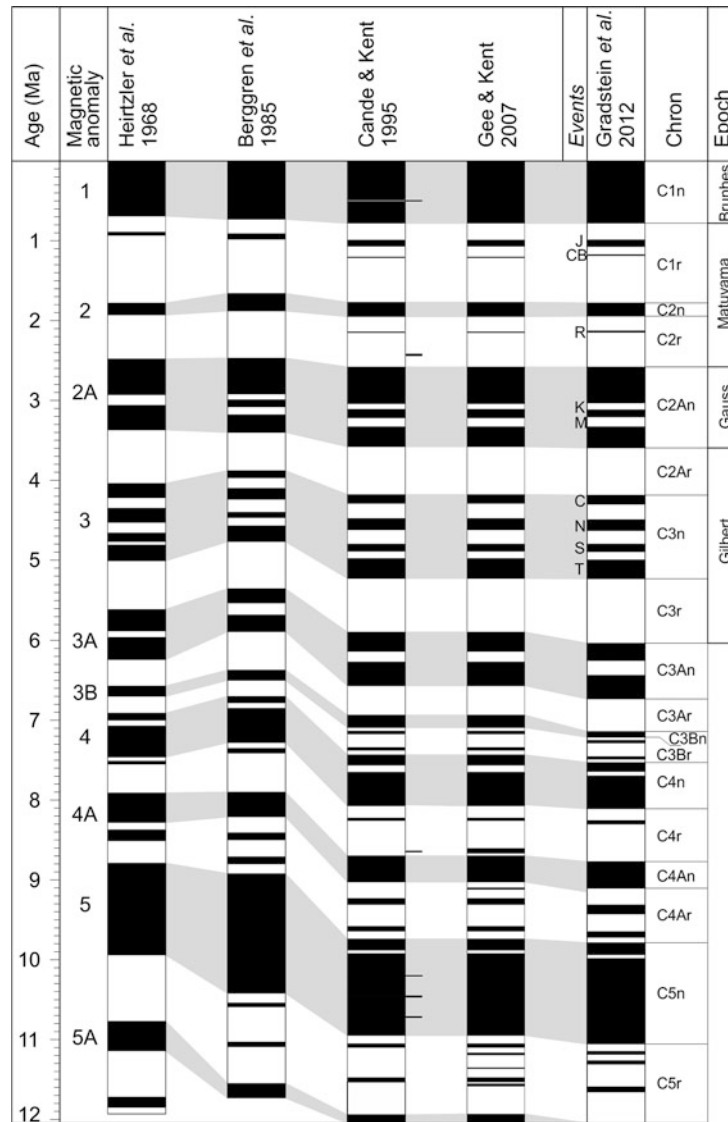


Fig. 1 Development of the geomagnetic polarity time scale of the last 12 Ma since marine magnetic anomaly patterns was first studied (Heirtzler et al. 1968). The convention is that periods of normal polarity are represented in black and reversed in white. *Short lines* to the right of the Cande and Kent (1995) polarity column correspond to cryptochrons. Event names are J (Jaramillo), CB (Cobb Mountain), R (Reunion), K (Kaena), M (Mammoth), C (Cochiti), N (Nunivak), S (Sidufjall), T (Thvera)

nine tie points for age calibration of the GPTS for the Late Cretaceous and Cenozoic. More recent calibrations have included astronomical ages of geomagnetic reversals of the Pliocene (Cande and Kent 1995), the Neogene (Gradstein et al. 2004), and Paleogene (Gradstein et al. 2012) (Fig. 2). It is expected that future developments of the GPTS will include astrochronological information of progressively older ages (Hinnov and Ogg 2007). In order to improve on both accuracy and precision of age calibration, important efforts for synchronization of the radiometric and astronomic time are needed (Kuiper et al. 2008).

Seafloor magnetic anomalies provide a quasi-continuous record of geomagnetic reversals. However, in the deconvolution of the magnetic anomaly signal into a polarity sequence, a resolution limit exists which depends on the depth and thickness of the magnetized layer in the oceanic crust. In general terms, geomagnetic chrons of 10^5 kyr duration are well represented in anomaly profiles

acquired from the sea surface. But even better resolution may be achieved in high-resolution profiles from fast-spreading ridges (>90 km/Myr), where short polarity intervals of few 10^4 year duration can be recognized (Gee and Kent 2007). Cande and Kent (1992) coined the term “cryptochron” to refer to magnetic anomalies which are too short to be unequivocally interpreted as true reversals. Further evidence for short chrons not yet present in the time scale can be obtained from high-resolution magnetostratigraphic records (Channell et al. 2003; Krijgsman and Kent 2004). At present, stability of the GPTS is not reached at this level of resolution, and it is expected that more cryptochrons will be elevated in the future to the category of new subchrons.

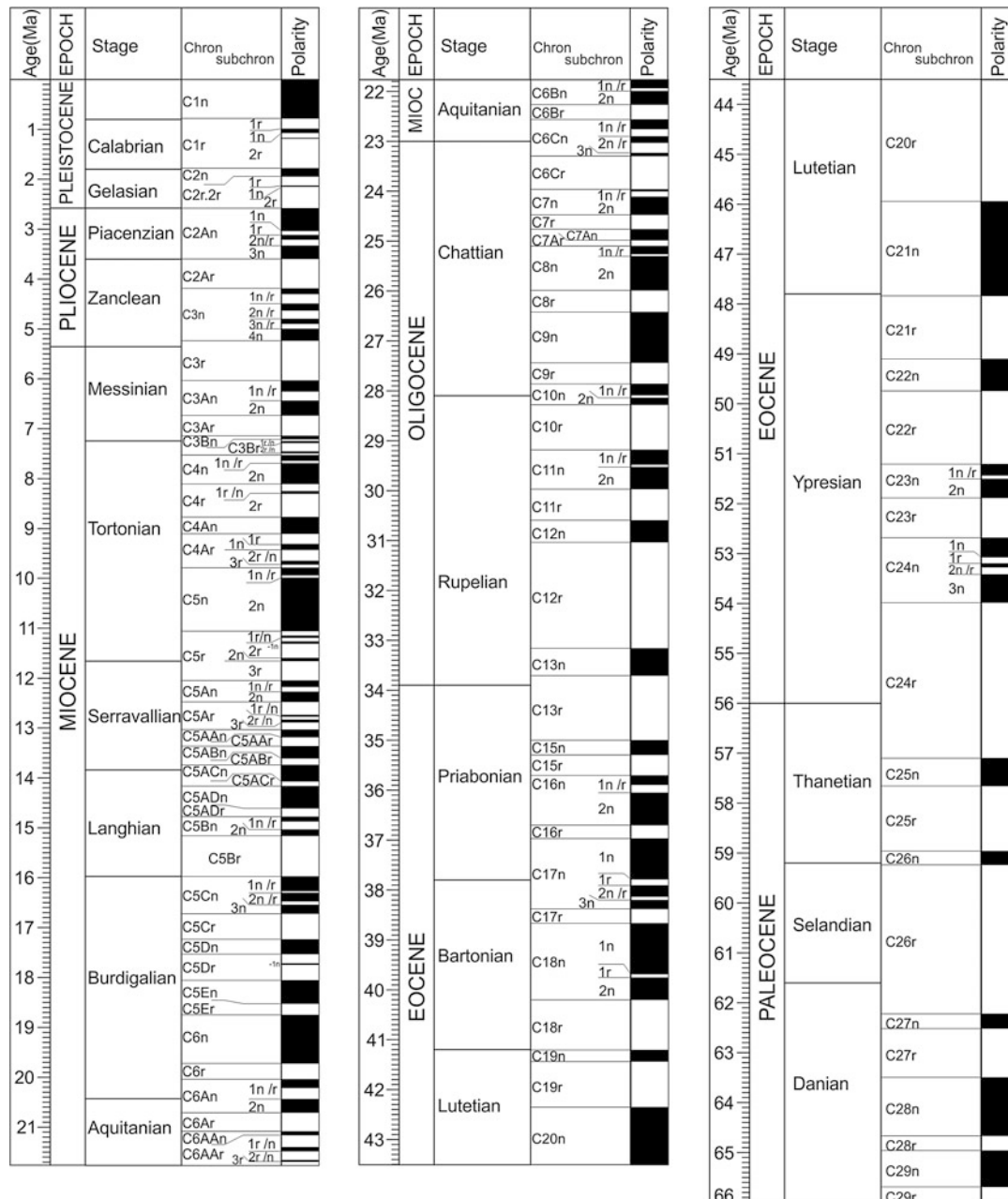


Fig. 2 Geomagnetic polarity chron zonation included in the last version of the geological time scale of Gradstein et al. (2012) and detailed nomenclature adopted from Cande and Kent (1992)

The occurrence of geomagnetic reversals follows a random pattern with no signs of periodicity. This indicates that geomagnetic reversal is essentially a process free of memory. And it is precisely the random and global character of geomagnetic reversal which makes magnetostratigraphic zonations useful for long-distance correlations. The age resolution of magnetostratigraphy depends on the average frequency of geomagnetic reversals, which has not remained stable through geological time (Gee and Kent 2007). The best resolution is achievable for the last 30 Ma, when the mean duration of geomagnetic chrons was 0.25 Ma, increasing to 0.75 Ma for ages between 30 and 80 Ma. On the other hand, magnetostratigraphy is inadequate for some quiet long periods when no reversals occurred, or one polarity dominated, such as the Cretaceous Normal Superchron (121–83 Ma) and the Carboniferous-Permian Reversed Superchron (310–265 Ma) (Langereis et al. 2010).

The Local Magnetostratigraphy

Sampling

A magnetostratigraphic study requires that suitable lithologies are sampled at approximately regular intervals. In principle, clay/silty sediments are best candidates to carry a primary remanence because stable magnetization is carried by small magnetic particles within the sub- μm size range. Coarser sandy sediments may yield good results as long as they contain significant amounts of clay matrix. Low-permeability fine-grained sediments are also preferred because they are less affected by later fluid flow and related remagnetization processes. As rock alteration processes can add secondary spurious magnetizations, fresh outcrops are highly recommended for paleomagnetic sampling. Some lithologies, such as organic-rich soft sediments, are prone to undergo alteration after sampling. In these cases, sample refrigeration may help preservation of their magnetic properties.

Paleomagnetic samples are taken in the field using either a water/air cooled portable drill or a hand sample. In soft sediments, the use of a hand pick is often required to dig down to fresh material. Drilling cores in situ is recommended because it is faster and simplifies sample preparation work in the laboratory. Electric-, rather than gasoline, powered drills are more appropriate for sampling unconsolidated soft sediments. In all cases, samples must be oriented before they are removed from the outcrop in order to calculate directions in geographic coordinates. In the case of tilted strata, bedding orientation data is needed in order to restore paleomagnetic vectors into tilt-corrected coordinates.

An optimal sampling resolution for magnetostratigraphy is such that allows recovery of all geomagnetic reversals recorded in the rock sequence. Available age constraints help constraining the most appropriate sampling density, although other factors such as field logistics, outcrop accessibility, and availability of suitable lithologies determine the sampling resolution finally achieved. Special care must be taken at this stage, since an incomplete sampling may give a polarity zonation that is unrepresentative of the true pattern of reversals.

Drill cores from marine and lacustrine unconsolidated sediments often provide unaltered material suitable for paleomagnetic measurements. Leading technologies used in scientific drilling have made possible full core recovery in soft sediments, providing the best material for very detailed magnetostratigraphic studies, where the resolution limit is marked by the sample size (7 cm^3) or, for continuous core measurements, the width of the response function of the magnetometer pick-up coils. In addition, advanced tools exist that provide azimuthal orientation to core samples, thus allowing full correction of paleomagnetic vectors into geographic coordinates.

Laboratory Processing

The NRM of samples is measured in the laboratory with rock magnetometers specially designed for paleomagnetic applications. Superconducting rock magnetometers are best suited for magnetostratigraphy because of their adaptability to standard paleomagnetic samples, cores, and U-channel samples. They provide the highest sensitivity and best performance with in-line automated measuring routines. An alternative instrument is the inexpensive spinner magnetometer, which has sufficient sensitivity to measure many sedimentary rocks, but requires more careful sample preparation and handling.

Treatment of paleomagnetic samples in the laboratory is oriented at identifying the different components contributing to the NRM. Widely applied techniques include stepwise thermal (TH) and alternating field (AF) demagnetization (Butler 1992; Langereis et al. 1989). Sample demagnetization is achieved by keeping the samples in a low-field environment, typically less than 10 nTesla, while subjected to TH or AF treatment. Complete thermal demagnetization is accomplished after exposure to a number of increasing temperature steps, until the maximum unblocking temperature of magnetic carriers is reached. Assuming that every NRM component is carried by a different population of magnetic grains, an effective isolation of components is achieved if their unblocking temperature spectra do not overlap significantly. TH demagnetization is optimal for removing secondary components carried by hydroxides such as goethite, because of its low unblocking temperature (Table 1). Thermal separation of fine-grained hematite and magnetite components needs closely spaced temperature steps because of the overlap of their stability fields. Alternatively, AF demagnetization successfully isolates magnetite from hematite components because they exhibit a large contrast in coercivity. Ideally, a set of pilot samples of representative lithologies is both TH and AF demagnetized, so that a specific demagnetization protocol can be designed for each case study.

Among the NRM components isolated after stepwise demagnetization, the most stable and consistent component is referred to as the Characteristic Remanent Magnetization (ChRM). Principal component analysis (Kirschvink 1980) is used to calculate the orientation of the ChRM, which is expressed with their values of declination (azimuth) and inclination (dip). By application of the geocentric axial dipole hypothesis, and given a site location on the Earth's surface and the orientation of a paleomagnetic component, the latitude of the corresponding virtual geomagnetic pole (VGP) can be calculated (Butler 1992; Tauxe 1998). Northern hemisphere VGP latitudes (positive) correspond to normal polarity and southern hemisphere latitudes (negative) to reversed polarity. A local magnetic polarity stratigraphy can be constructed after plotting VGP latitudes as a function of stratigraphic position of samples (Fig. 3).

Paleomagnetic data from drill cores not azimuthally oriented can be used for magnetostratigraphic purposes as long as the drill hole is perpendicular to bedding. Information of magnetic polarity is then given by the vertical component (Z) of magnetization. In this case, special attention must be given to the latitude at which the sediments originated; the Z component tends to zero at equatorial latitudes, and its sign is no longer a good indicator of polarity. At low latitudes, azimuthal orientation of cores is needed because information of magnetic polarity is best extracted from the paleomagnetic declination.

The reliability of a given magnetostratigraphy relies on, first, the demonstrable primary nature of the ChRM and, second, the completeness of the polarity sequence. To assess the age of the magnetization, some stability tests (fold test, conglomerate test, consistency test, and reversal test) can be carried out (Butler 1992; Opdyke and Channell 1996; Tauxe 1998). The fold test provides information on the timing of magnetization relative to folding. A fold test is positive if paleomagnetic directions from opposing flanks of a fold converge after tilt correction. A positive fold test

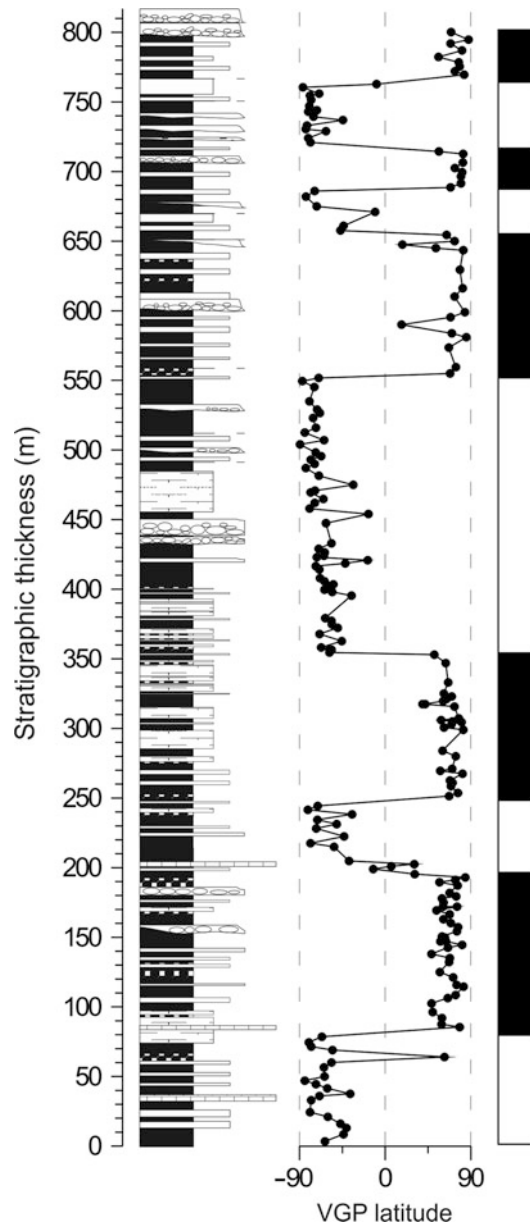


Fig. 3 Magnetostratigraphy of the Librilla section, Fortuna basin, Spain (Garcés et al. 2001). A polarity sequence is determined from the Virtual Geomagnetic Pole latitude, positive VGP latitudes represent normal polarity, and negative VGP latitudes reverse polarity

indicates that remanence predates folding, but does not strictly demonstrate a primary (syndimentary) origin as required for magnetostratigraphy. Only in cases of early syndimentary folding, or slumped sediments, a positive fold test provides greater confidence on the primary origin of the magnetization. The conglomerate test assesses the stability of the magnetization measured from intraformational clasts. Random paleomagnetic directions from different clasts indicate that the magnetization has not been reset since the clasts were reworked from its original strata, thus yielding a positive test. The consistency test is applied for multiple overlapping magnetostratigraphic sections. A sequence of reversals that can be traced laterally, and cross-checked with lithostratigraphy, gives the strongest evidence of a primary magnetization. The reversal test is used to check for antipodality of the average normal and reversed paleomagnetic directions. A failed reversal test

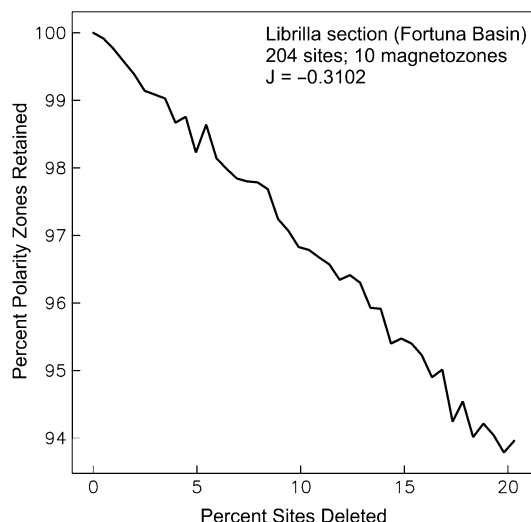


Fig. 4 Magnetostratigraphic jackknife of the Librilla section. A J value between 0 and -0.5 indicates that the probability of missing magnetic reversals due to sampling resolution is low

indicates that stepwise demagnetization has not succeeded in fully isolating discrete magnetic components. Passing the reversal test is critical for studies in which the angular deviation from a reference paleomagnetic direction is used to interpret tectonic rotation of rock units. On the other hand, the reversal test is not so crucial for magnetostratigraphy since the magnetic polarity can be often assessed from partially overlapped paleomagnetic directions.

Assessing Completeness of Local Magnetostratigraphy

A magnetostratigraphic section is considered complete when the sampling density is enough to support that no geomagnetic reversals are missed between sampled horizons. Note that, in this sense, magnetostratigraphic completeness is different from stratigraphic completeness, the latter referring to the occurrence and duration of sedimentary (=time) gaps. Completeness of local magnetostratigraphy can be statistically assessed by different means. The dependence of a given magnetic polarity sequence on sampling strategy was investigated by Johnson and McGee (1983), who concluded that polarity sequences yielding an average of 8 sites/magnetozones are insignificantly affected by sampling bias. Tauxe and Gallet (1991) proposed a statistical jackknife in order to test magnetostratigraphic completeness. The sensitivity to sample resolution is described by a parameter J , which represents the slope relating the percentage of magnetozones missed after a random and progressive deletion of samples up to 20 % of the total number of samples (Fig. 4). These authors recommend J ranges between 0 and -0.5 , lower values indicating that the section was insufficiently sampled.

Magnetostratigraphic Correlation

The random character of geomagnetic reversals originates a distinctive polarity sequence when a sufficient length of time is observed, which depends on the average frequency of reversals. For Neogene times, it can be estimated that a stratigraphic sequence spanning about 3 Myr will reveal a magnetic polarity sequence of 10–15 reversals, an adequate number to assess a correlation. A correlation with the geomagnetic polarity time scale (GPTS) is achieved if the pattern of magnetozones finds a positive match with a sequence of reversals in the GPTS. In achieving this,

absolute ages of geomagnetic reversals can be assigned to every magnetozone boundary in the local stratigraphy.

Magnetostratigraphic correlation with the GPTS is often assisted by absolute age constraints, for example, radiometric ages from interstratified ash layers or lava flows, or biostratigraphic data which may provide chronostratigraphic information at stage level or better. But attention must be paid to the diverse sources of error associated to external age constraints. In the case of radioisotopic dating, only the analytical precision (often less than 0.5 %) is propagated into the error reported (Renne 1998). Radioisotope decay constant uncertainties and other sources of systematic errors, which are often unnoticed by non specialists, are particularly problematic when different isotopic systems are combined, as occurs in the calibration of the GPTS. A recommended practice is that best correlation is searched within a time range only approximated by external age constraints, but not forced by a single tie point of presumed high accuracy. A correlation which is not supported by a positive match of the magnetostratigraphic pattern and is solely substantiated on an external age constraint must be taken with caution.

Achieving a robust correlation between a local magnetostratigraphy and the GPTS requires that sedimentation rates do not change significantly at the time scale of geomagnetic chrons, so that the relative thickness of magnetozone maintains proportionality with the duration of corresponding geomagnetic chrons. From a sedimentological perspective, sedimentation steadiness may appear as severe restriction for magnetostratigraphic correlation, particularly in continental settings dominated by alluvial/fluvial processes of clearly episodic nature. A compilation by Sadler (1981) showed that for typical durations of chrons (10^4 – 10^6 year), average accumulation rates of fluvial sediments may vary by three orders of magnitude. The scattering, however, partially responds to the diverse geologic (tectonic, paleogeographic, climatic) settings from which the database was constructed. Observations restricted to a specific setting and location result in sedimentation rates which cluster to within an order of magnitude (Fig. 5a), as already observed by (Johnson et al. 1985) in the Siwaliks Himalayan foredeep. More important for correlation purposes is the relative change of sedimentation rate between adjacent magnetozone. Observations from the alluvial sequences of the Ebro Basin shows that sedimentation rates rarely change by a factor greater than 2 between two adjacent chrons, while the relative duration of adjacent chrons of the GPTS varies over an order of magnitude

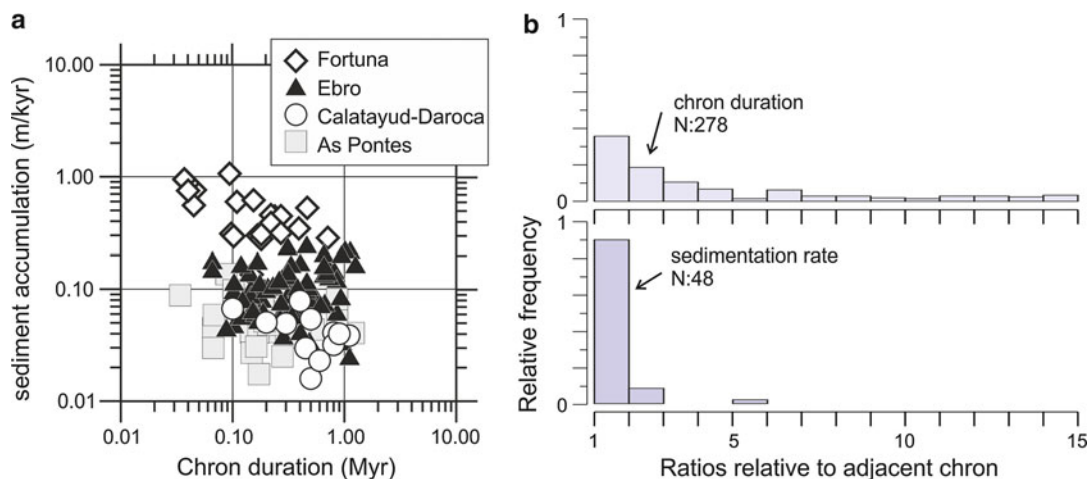


Fig. 5 (a) Average sedimentation rates in continental sediments as a function of time span of observation (duration of chron) (Data from magnetostratigraphic studies in Cenozoic basins of Spain). Note that sedimentation rates cluster to an order of magnitude when data from a single basin is considered. (b) Ratio of duration of adjacent chrons in the Cenozoic compared to ratios of sedimentation rates of adjacent chrons (Data from the Ebro Basin)

(Fig. 5b). These observations lead to the conclusion that changes in sedimentation rate rarely originate an excessive mismatch between the local magnetostratigraphy and its equivalent reversal sequence in the GPTS (Fig. 6).

In the long term ($>10^7$ year), average accumulation rates are fundamentally constrained by basin forming mechanisms and the resulting balance between sediment yield and accommodation space. At this scale, significant changes of the tectonic, paleogeographic, and/or paleoclimatic setting may lead to gradual or even abrupt changes in the sedimentation trends. Fortunately, periods of sedimentary reorganization, which impact on a specific site location, are few compared to times of stability. The result is that evolution of basin infill often reveals long periods of steady sedimentation, these being interrupted by short periods of change (Fig. 7). Under these circumstances, unambiguous magnetostratigraphic correlation with the GPTS, independent of external age controls, is still an achievable goal.

Assessing Overall Reliability

Assessment of the overall reliability of magnetostratigraphic dating was addressed by others (Talling and Burbank 1993), who analyzed all sources of error associated with absolute ages derived from magnetostratigraphy and quantified error magnitudes related to the accuracy of the GPTS and the completeness of the local magnetostratigraphy. But, uncertainties involved in nonunique correlations could only be qualitatively treated. In this respect, it is recommended that an explicit discrimination is made between correlations based on an external (biostratigraphic or radiometric) age control and those based on the smoothest-derived sediment-accumulation rates. There are cases that a best-fit magnetostratigraphic correlation does not meet other external age constraints (Fig. 6). At this point, magnetostratigraphic correlation becomes a multidisciplinary approach which involves a proper analysis of all sources of uncertainty.

A reliability index for magnetostratigraphic data was put forward by Opdyke and Channell (1996) based on criteria listed below, with the recommendation that ratings of 5 (out of 10) should be achieved:

1. Biostratigraphic data provides an age control at the level of stage.
2. Sampling localities placed in a measured stratigraphic section.
3. Complete stepwise NRM demagnetization of all samples.
4. Paleomagnetic directions determined by least-square analysis.
5. Numerical data fully documented with plots of VGP latitude against stratigraphic position (or declination and inclination).
6. Determination of magnetic mineralogy.
7. Use of field tests (fold test, conglomerate test) to determine the stability and age of the magnetization.
8. Reversal test, to check for the overlap with secondary magnetizations.
9. Radiometric ages are available for the section and fully documented with their associated errors.
10. Consistency test, to check for the stratigraphic control of polarity reversals, and the primary nature of the magnetization.

Among these, criteria 2, 3, 4, 5, and 6 are standardized procedures in modern magnetostratigraphic studies and should be mandatory for proper publication of results. Other criteria, such as availability of external age controls (1 and 9) and stability tests (7, 8, and 10), are case dependent and cannot always be met.

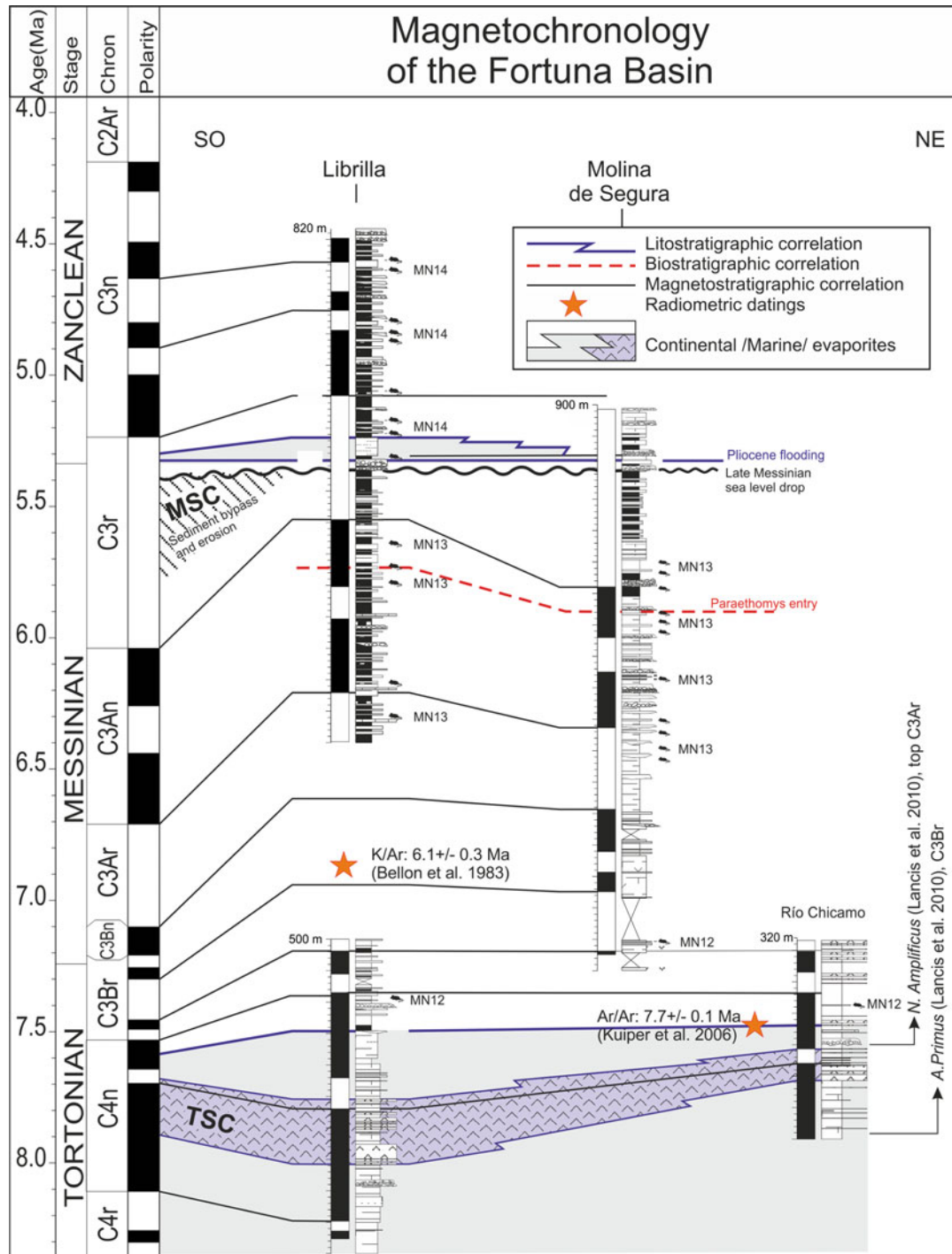


Fig. 6 A magnetochronology of the Fortuna basin infill based on multiple magnetostratigraphic sections (Garcés et al. 2001). Basin scale correlations are guided by both lithostratigraphic boundaries (diachrony allowed) and biostratigraphic markers (MN12, MN13, MN14 correspond to European mammal zones). A magnetostratigraphic correlation between overlapping sections yields a positive consistency test, supporting a primary magnetization. The resulting composite magnetostratigraphy is made of 19 magnetozones (10 Normal, 9 Reverse), with a pattern of reversals which allows unambiguous and independent correlation with the GPTS. Note that some external (biostratigraphic and radiometric) age constraints do not match with the proposed correlation. In particular, K/Ar data of the Barqueros volcanism (Bellon et al. 1983) and calcareous nanoplankton from the Rio Chicamo (Lancis et al. 2010) suggest an age >1Myr younger for the lower marine units. On the other hand, the Ar/Ar dating of the Cabezos Negros

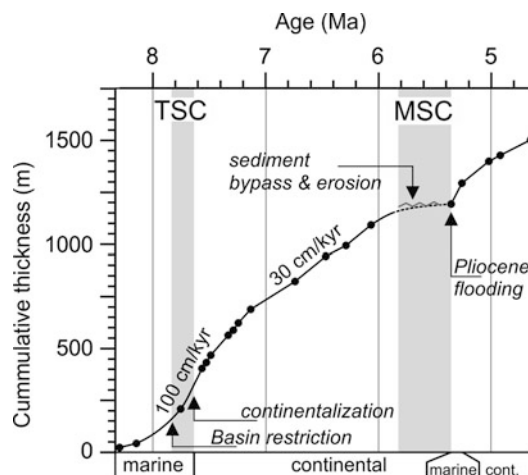


Fig. 7 Sedimentation rates in the Fortuna basin derived from magnetostratigraphic correlation (Fig. 6). The basin underwent a complex evolution, with a paleogeography which rapidly changed from open marine to a restricted elongated gulf and, finally, continental environments eventually altered by the sea level drop of the Mediterranean during the MSC. Despite this unfavorable scenario, periods of steady sedimentation in the Fortuna basin are long enough to support a preferred magnetostratigraphic correlation

Conclusions

Magnetostratigraphy is challenging among the different dating methods of sedimentary rocks, because the outcome is not as simple as determining a numerical age with its associated error. A correlation is established between a local magnetic polarity zonation and the globally isochronous geomagnetic reversals of the GPTS, whose age calibration relies on absolute chronometers, such as radioactive dating and astrochronology. Thus, a recommended practice is that magnetostratigraphic ages are not only expressed with its derived numerical value but as a correspondence with geomagnetic chron boundaries. Popularity of magnetostratigraphy as a dating tool relies on the fact that many sedimentary rocks are faithful recorders of the ancient magnetic field and that modern magnetometers are capable of measuring very weakly magnetized samples. On the other hand, the inadequacy of magnetostratigraphy to be applied to discontinuous or very short sedimentary records remains as the fundamental limitation. A full comprehension of the regional stratigraphic context and accessibility to long and continuous sedimentary sequences is crucial for magnetostratigraphy to contribute robust and independent age constraints.

Fig. 6 (continued) volcanism (Kuiper et al. 2006) supports the proposed magnetostratigraphic correlation. The Tortonian Salinity Crisis (TSC) corresponds to a tectonic-driven basin restriction event which caused the precipitation of evaporates in the Fortuna and Lorca basins (Krijgsman et al. 2000). The Messinian Salinity Crisis (MSC) of the Mediterranean culminated with a base level drop which caused erosion of the Mediterranean peripheral margins. The MSC in the Fortuna basin caused fluvial incision which was later flooded during the Pliocene transgression (Garcés et al. 2001)

Cross-References

- [Magnetic Anomalies](#)
- [Magnetic Chronology](#)
- [Magnetism, Rock and Mineral](#)
- [Magnetometer](#)

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Rb–Sr Dating

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Synonyms

[Rb–Sr geochronology](#)

Definition

Parent–daughter ratio: The ratio of rubidium (Rb) to strontium (Sr). The ratio is commonly expressed as $^{87}\text{Rb}/^{86}\text{Sr}$, where the unstable Rb-87 isotope is referred to as the parent nuclide, being approximately 27 % of all rubidium. The daughter nuclide (Sr-87) is represented by Sr-86, which is stable and not subject to radiogenic ingrowth and constitutes approximately 9.9 % of all strontium.

Nicolaysen diagram: A diagram of Rb-87 (abscissa) versus Sr-87 (ordinate), both normalized to Sr-86 (expressed as $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) illustrating the effect of age on the radiogenic decay of Rb-87 to Sr-87.

Initial isotope equilibrium: The assumption that at the time of formation of a rock, all phases therein share the same Sr isotope composition; a prerequisite for an isochron.

Isochron: A best-fit line of three or more phases in a Nicolaysen diagram with its slope corresponding to an age of phases that are in initial isotope equilibrium. Two-point isochrons may be used and can have geologic significance but do not allow constraints on their reliability.

Errorchron: A median through three or more phases in a Nicolaysen diagram that do not plot on a single regression line within the limits of their uncertainty. An age corresponding to the slope of this median may have geologic relevance but cannot be treated as an actual geologic event.

Isochron initial: Common expression of the intercept of the isochron with the ordinate in a Nicolaysen diagram that marks the strontium isotope composition at the time of formation which, by definition, is that of all phases contributing to the isochron.

MSWD: Mean square of weighted deviates; a value describing the degree of correlation of individual points on an isochron with an ideal value of 1.

Historical Background

The Rb–Sr dating technique is among the most widely used and most powerful dating tools available in Earth sciences. It is an effective means of dating igneous rocks or metamorphic events and, under special circumstances, can be applied to sedimentary sequences, ore deposits, and past volcanic eruptions or to date fluid events in the deep crust. The natural radioactivity of Rb-87 was discovered by Campbell and Wood (1906) and first described as a dating technique by radiochemist pioneer

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Table 1 Relative abundances of the stable isotopes of Sr (average atomic mass of 87.62 ± 1) and Rb (average atomic mass of 85.4678 ± 3) and the radioactive isotope Rb-87 (De Laeter et al. 2003). Note that relative abundances of Sr are variable in individual reservoirs due to the radiogenic ingrowth of Sr-87. All uncertainties refer to the last significant digit

Strontium (Sr)		Rubidium (Rb)	
Sr-84	0.0056 ± 1		
—		Rb-85	0.7217 ± 2
Sr-86	0.0986 ± 1		
Sr-87	0.0700 ± 1	Rb-87	0.2783 ± 2
Sr-88	0.8258 ± 1		

Otto Hahn (Hahn et al. 1943; Hahn and Walling 1938). Subsequent improvements in precision and accuracy have contributed significantly to a better understanding of Earth's history.

With the advent and distribution of mass spectrometers, the Rb–Sr technique has become the most important tool in dating igneous rocks throughout Earth's history and to the infant stages of the solar system. It has been used to date meteorites (e.g., Minster and Allègre 1976; Minster et al. 1982; Misawa et al. 1993), was among the first dating techniques applied to lunar samples returned from the Apollo missions (e.g., Murthy et al. 1971; Papanastassiou and Wasserburg 1970; Papanastassiou et al. 1970), and has identified the oldest rocks of Earth (e.g., De Laeter et al. 1985; Hurst et al. 1975; Moorbath et al. 1977a, b). Hence, Rb–Sr dating has greatly contributed to developing an emerging idea of our environment: an evolving and ever changing planet.

In recent years, the Rb–Sr dating technique has lost some of its popularity to other dating tools. Other chronometers, such as U–Pb in zircon, can, in principle, date similar events to higher precision and, in the case of high-temperature igneous emplacement events, higher accuracy. Nonetheless, taking the properties of alkali and alkaline earth elements into account, and refinements in analytical techniques for Rb–Sr, it remains a powerful tool to date rocks and metamorphic assemblages and is re-establishing its place among the top dating techniques.

The Concept of Rb–Sr Dating

Rb–Sr dating is based on the radioactive decay of the isotope Rb-87 (that today accounts for ~28 % of all rubidium) to Sr-87 (~7 % of all strontium, Table 1) by beta decay, i.e., the emission of an electron. Rb-87 decays to Sr-87 with a half-life of approximately 49 billion years. This makes the Rb–Sr dating technique, in principle, suitable to date samples from the infant stages of the solar system to very recent igneous events, i.e., a few million years before present.

For dating with the Rb–Sr technique, at least two phases (either whole rocks or minerals) with different Rb–Sr ratios are required. To directly compare Sr isotope compositions of these phases, irrespective of their absolute amount of Rb and Sr, all Sr-87 values are reported relative to a stable Sr isotope (Sr-86) that is not subject to radiogenic ingrowth. Thus, all Sr isotope compositions are reported as $^{87}\text{Sr}/^{86}\text{Sr}$; $^{87}\text{Rb}/^{86}\text{Sr}$ ratios are reported accordingly as $^{87}\text{Rb}/^{86}\text{Sr}$ following the equation:

$$\frac{A(\text{Rb-87}) \times M(\text{Rb}) \times [\text{ppm Rb}]}{A(\text{Sr-86}) \times M(\text{Sr}) \times [\text{ppm Sr}]} \quad (1)$$

where A is the relative abundance, M the atomic mass, and [ppm] the concentration of a species, usually given in parts per million. The amount of radiogenic ingrowth of Sr-87 in at least two phases with different Rb–Sr corresponds to the amount of decayed Rb-87. With knowledge of the exact decay rate (the Rb decay constant, $\lambda^{87}\text{Rb}$), this enables the calculation of radiogenic ingrowth and

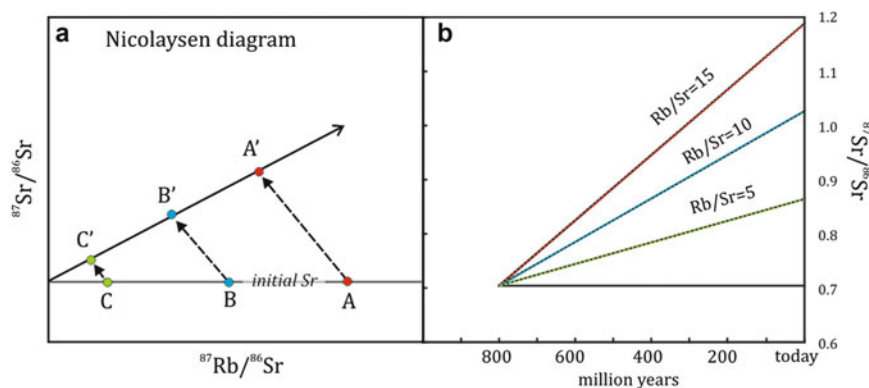


Fig. 1 (a) $^{87}\text{Rb}/^{86}\text{Sr}$ isochron diagram (Nicolaysen 1961); showing the time-dependent evolution of three different phases, (A–C) with variable $^{87}\text{Rb}/^{86}\text{Sr}$ that formed in initial isotopic equilibrium and thus have the same initial Sr isotope composition. Points A'–C' reflect the present-day isotope composition of phases A–C, as measured by mass spectrometry. (b) The same isotope evolution in an Sr isotope versus time plot with the relative evolution of the three different phases as a consequence of their variable $^{87}\text{Rb}/^{86}\text{Sr}$

ultimately, by integrating both phases, the time required for this decay. This relationship is displayed in Fig. 1, where three phases with different $^{87}\text{Rb}/^{86}\text{Sr}$ (A, B, and C) start with the same Sr isotope composition and with time evolve to different $^{87}\text{Sr}/^{86}\text{Sr}$ (A', B', and C'), based on their $^{87}\text{Rb}/^{86}\text{Sr}$. Today, these phases plot on a regression line (within analytical uncertainty), which is usually highlighted by an MSWD ~ 1 .

The isotope composition of a sample after a given time t is expressed by the decay equation:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}}(t) = \frac{^{87}\text{Sr}}{^{86}\text{Sr}}(t_0) + \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda t} - 1) \quad (2)$$

where $^{87}\text{Sr}/^{86}\text{Sr}(t_0)$ is the initial isotope composition at a time t_0 . If two or more Sr isotope compositions and their $^{87}\text{Rb}/^{86}\text{Sr}$ are known, a time interval Δt ($t_1 - t_0$) and the Sr isotope composition at t_0 can be calculated using a Nicolaysen diagram (Nicolaysen 1961), where the age difference Δt (or simply t) corresponds to the slope of the regression line through those samples. Ideally more than two samples are used for this concept to ensure that the regression line indeed reflects an age; the more samples that are used in a Nicolaysen diagram plot, the more likely it is that the regression is geologically meaningful. Obviously, for two samples a regression can be calculated, even though both samples may not be related to each other, rendering any calculated age (or initial isotope composition) of such “two-point” isochrons potentially dubious without any independent age indicators.

Analytical Techniques and Limitations

The precision of an age derived from an isochron is controlled by (i) the number of points used to obtain a regression line, (ii) the spread in $^{87}\text{Rb}/^{86}\text{Sr}$, (iii) the degree to which the phases involved formed in isotope equilibrium, and (iv) the errors on each individual analysis of $^{87}\text{Rb}/^{86}\text{Sr}$ and Sr isotope composition. Where the first three parameters are defined by the sample, the latter is a matter of analytical capability. Strontium isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}$) vary from subtle variations among whole rocks or mineral phases in the fifth decimal place (i.e., 0.0000X) to large variations, especially in older samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ can be routinely analyzed with high precision and accuracy in samples with >50 ng Sr by thermal ionization mass spectrometry (TIMS) to within 40 ppm. Modern TIMS instruments can achieve precisions that are far better (up to 5 ppm); however,

other sources of error usually result in poorer accuracy and higher external reproducibility, i.e., the variability in isotope compositions of a single sample from multiple analyses (including sample digestion). Error sources can include procedural contaminants (commonly referred to as “blank”) or isotope tracer calibrations. The procedural blank can be minimized to insignificant levels by the use of ultraclean reagents (e.g., distilled acids, de-ionised water, or purified chromatographic extraction resin) and by chemical purifications in a clean room environment, and modern laboratories generally fulfill this requirement.

The second parameter required for age determinations is the $^{87}\text{Rb}/^{86}\text{Sr}$, which is commonly determined by isotope dilution using an isotope tracer. To ensure accurate results for isochron relationships, the Rb–Sr of a sample should directly be determined in the same sample cut as the one used for Sr isotope analysis so that the amount of Rb directly corresponds to the radiogenic ingrowth of Sr. The method of isotope dilution is currently the most precise and accurate way to obtain this ratio in conjunction with Sr isotope analyses; a precision of ~0.1–0.2 % on $^{87}\text{Rb}/^{86}\text{Sr}$ values can be obtained. Alternative methods, e.g., using single-collector mass spectrometry with inductively coupled plasma source (ICP-MS), can be used, but currently yield much poorer precision (~3–5 %) on the elemental ratio. For isotope dilution, both Sr and Rb (resident in the same material) are doped with a mixed isotope tracer artificially enriched in one Sr and one Rb isotope, preferably a low natural abundance isotope. This “spike” is added to the sample prior to digestion to ensure full spike-sample equilibrium. Knowledge of the concentrations and isotopic compositions of the spike, coupled with accurate weights of sample and spike, can be used to calculate Rb and Sr concentrations. Spiked Sr isotopes are simultaneously analyzed with the radiogenic isotope composition; spiked Rb isotopes are analyzed individually. For this, both Rb and Sr must be separated from the rock matrix and from each other to avoid matrix effects during the isotope analyses and, more importantly, isobaric interferences of Sr-87 and Rb-87, which will both be detected as mass 87. The common method for this separation is chromatographic extraction of dissolved (and spiked) sample material.

The calibration of the isotope tracer, a prerequisite to ensure accurate determinations of $^{87}\text{Rb}/^{86}\text{Sr}$, is not straightforward for both Rb and Sr. Whereas for other radiogenic systems, such as U–Pb or Sm–Nd, metals can be weighed very accurately and used to prepare a well-characterized standard solution, Rb metal is highly reactive in the atmosphere and does not permit this approach. Alternatives are Rb salts, which must be dried prior to analyses (due to their hygroscopic nature) and stoichiometry must be assumed. A good example of a modern calibration of a Rb–Sr spike using different salts for cross-calibration is given in Nebel et al. (2011). A way to avoid interlaboratory bias due to different spike calibrations is through analyses of a Rb–Sr isotope standard. Unfortunately, there are currently not many well-characterized standards available. The most commonly used standard is the NIST-607 K-feldspar standard. There are several problems associated with K-feldspar (see below); however, Nebel and Mezger (2006) presented a possible solution using this standard to cross-calibrate isotope tracer solutions. To obtain the most accurate result and to eliminate error magnification by mixing disproportional spike-sample ratios, general knowledge of sample concentrations for both, Rb and Sr, is desirable and often different spikes with variable $^{87}\text{Rb}/^{86}\text{Sr}$ are used for high or low Rb–Sr phases, respectively.

The conventional method for Rb isotope dilution analysis is by thermal ionization mass spectrometry (TIMS). Mass spectrometric-induced isotope fractionation on a TIMS instrument can only be controlled to within 0.5–1 % for elements with only two stable isotopes, such as Rb, and for decades this has been a limiting factor in Rb–Sr chronology. Recent developments in multi-collector ICP-MS have enabled analyses of Rb isotopes to <0.1 % (Nebel et al. 2005; Waight et al. 2002a), which enables the determination of $^{87}\text{Rb}/^{86}\text{Sr}$ to a precision of ~0.2 % (Nebel and Mezger 2006;

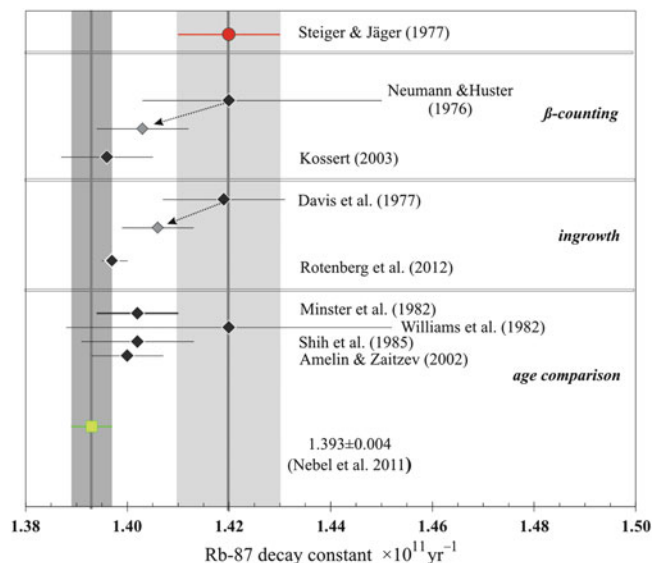


Fig. 2 Compilation of reported decay constants with details on the methods of determination (Modified after Nebel et al. (2011)). Gray dotted lines are recalculated values as reported in Begemann et al. (2001) (Data sources: Amelin and Zaitsev 2002; Davis et al. 1977; Kossert 2003; Minster et al. 1982; Neumann and Huster 1976; Rotenberg et al. 2012; Shih et al. 1985; Steiger and Jäger 1977; Williams et al. 1982)

Waight et al. 2002a), which corresponds to precisions achieved for other dating tools, as, e.g., Sm–Nd or Lu–Hf. In contrast to other dating methods, a major disadvantage for Rb–Sr dating is that no *in-situ* dating can be performed. To date, ion microprobe and laser ablation ICP–MS analyses, common *in-situ* techniques applied to date high U/Pb minerals, do not yield precise and accurate combined Sr isotope ratios and parent–daughter ratios in high $^{87}\text{Rb}/^{86}\text{Sr}$ phases required to obtain geologically significant ages (Vroon et al. 2008; Waight et al. 2002b). The major reason for this is the inability to adequately correct for the isobaric interference of Rb-87 on Sr-87.

The last key parameter to accurately date rocks and mineral assemblages with Rb–Sr is the decay constant ($\lambda^{87}\text{Rb}$). By successfully addressing all of the abovementioned parameters, a precision in Rb–Sr ages can be achieved that is comparable to other dating techniques. However, a systematic bias can be introduced by insufficient knowledge of the Rb decay constant (Begemann et al. 2001), i.e., the rate at which Rb decays. Recent efforts to refine $\lambda^{87}\text{Rb}$ have improved the precision and accuracy of the constant to $\pm 0.1\text{--}0.2\%$ (Nebel et al. 2011; Rotenberg et al. 2012); an error in the order of the analytical precision of the measurements (see Fig. 2 for a compilation of reported Rb-87 decay constants and their precisions). Accordingly, all ages in this article have been recalculated using an Rb-87 decay constant of $\lambda^{87}\text{Rb} = 1.393 \times 10^{-11}$ (Nebel et al. 2011). The value of $\lambda^{87}\text{Rb} = 1.42 \times 10^{-11}$, which was commonly used before this revision, was proposed in 1977 by an international commission on geochronology (Steiger and Jäger 1977). The revision of this value implies that all previously reported Rb–Sr ages are ca. 2 % older than previously thought.

Dating of Igneous Rocks (Including Volcanic Ash)

The most widely used application of the Rb–Sr dating technique is in determining the age of crystallization of igneous rocks. For this, either multiple whole rocks (with a genetic, often comagmatic relationship) or mineral separates from a single rock that formed contemporaneously are used to date the emplacement event. This implies that all species used for the dating share an

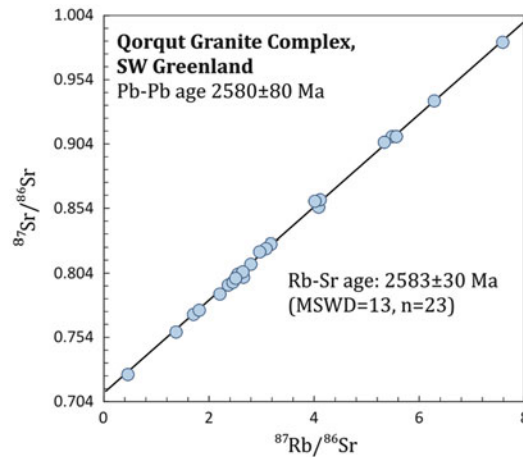


Fig. 3 Isochron diagram of whole rocks from a late Archean granite complex in Greenland (Moorbath et al. 1981). Rb–Sr and Pb–Pb yield identical results, and all rocks are presumably non-altered, indicating coherence of the isotope systems and an emplacement event at 2.58 ± 0.03 Ga

identical Sr isotope composition at the time of formation. Rock suites and minerals need to be carefully evaluated to fulfill this criterion, which is often not the case (Field and Raheim 1979), or to assess subsequent alteration by secondary processes. Examples of such cases are detailed below. However, in the ideal case of isotope coherence between samples and further textural or petrogenetic evidence for an igneous origin of a rock, an age for a suite of samples can be calculated. For this, in the isochron diagram of Fig. 1a, the dashed lines correspond to a family of lines leading from A to A', B to B', and so on, with the equation

$$y = mx + n \quad (3)$$

where all x–y coordinates in a Nicolaysen diagram plot as points on a straight line: the isochron. In this diagram the following parameters define the age: $x = {}^{87}\text{Rb}/{}^{86}\text{Sr}$ and $y = {}^{87}\text{Sr}/{}^{86}\text{Sr}(t)$ for any given sample, and $n = {}^{87}\text{Sr}/{}^{86}\text{Sr}(t_0)$ or initial ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ is common to all samples. The age t (in years) of the suite of samples then corresponds to the slope m of this isochron with

$$m = e^{\lambda t} - 1 \quad (4)$$

The initial ratio n is the intercept of the isochron with the ordinate; λ is the Rb-87 decay constant. Obviously, two or more co-genetic species are required for this dating method. An example for one of the first dating attempts of a suite of Archean igneous whole rocks from the Qorqut igneous complex in Greenland (Moorbath et al. 1981) is presented in Fig. 3. These samples, assumed to be in initial isotope equilibrium, correspond to a calculated age that is similar to the Pb–Pb age of the same samples, noting that the MSWD of this example indicates some isotope disturbance and thereby technically is an errorchron (MSWD ~ 13).

Other samples that are seemingly in isotope equilibrium (assuming no post-emplacement disturbance) are volcanic ash horizons. These represent important time markers in the Phanerozoic era because of (i) mineral species that allow precise dating and (ii) their widespread spatial distribution that allow correlations of stratigraphic horizons. Although U–Pb in zircon is the most precise and commonly used method to date these events with extremely precise resolution on timescales of thousands of years in Quaternary eruptions (Crowley et al. 2007), Rb–Sr is, in principle, applicable

to dating of volcanic ash (Lanphere and Baadsgaard 2001). Ash often contains apatite, K-feldspar, and biotite, which, in combination, share a large spread in $^{87}\text{Rb}/^{86}\text{Sr}$ and are thus ideally suited for Rb–Sr dating. However, in agreement with high-precision U–Pb analyses of zircon and titanite from tuff (Schmitz and Bowring 2001), Rb–Sr on single grains from the Fish Canyon Tuff, an enormous volcanic eruption approximately 28 Ma ago and often used as a dating standard in $^{40}\text{Ar}/^{39}\text{Ar}$ chronology, has revealed that Rb–Sr systematics can yield different age information. This difference may reflect crystal residence times in the underlying magma chamber prior to eruption or that some crystals are xenocrysts, i.e., assimilated from other sources, and are thereby not in isotope equilibrium with the host melt (Charlier et al. 2007), as is so often observed for U–Pb in zircon. In young volcanic systems where timescales of magma storage contribute more substantially to the absolute age, this can be problematic and needs to be carefully evaluated to obtain precise and accurate times of eruption. This is of particular importance for cross-calibration of geochronologic tools. However, in older systems, a pristine sample suite provided, precise and accurate Rb–Sr ages on bentonites are a useful alternative to U–Pb or $^{40}\text{Ar}/^{39}\text{Ar}$ dating in obtaining absolute ages of key stratigraphic horizons in Earth's history (Baadsgaard et al. 1988; Williams et al. 1982). This can be expected to be more important in future studies, especially in light of recent analytical improvements of Rb–Sr dating of mica as an alternative to $^{40}\text{Ar}/^{39}\text{Ar}$ dating (Willigers et al. 2004).

Isotope Mixing Versus Isochron Relationship

A potential complication for accurate age determinations of igneous rocks with the Rb–Sr technique may result from the mixing of two isotopically distinct magmatic reservoirs at or close to the time of emplacement, where isotope equilibrium is not achieved prior to crystallization. Isotope mixing between two reservoirs cannot easily be identified in a magmatic suite without additional age constraints or other petrologic genetic information. Mixing of the two end-members produces a straight line in an isotope evolution diagram, because both abscissa and ordinate are normalized to the same isotope ($\text{Sr}-86$). Mixing thus mimics isochron relationships and indicates an age that is older than the actual igneous-rock-forming event. This is particularly important for bulk rock analyses where geochemical heterogeneity can be preserved more easily than for mineral species derived from a single sample. This effect is illustrated in Fig. 4a for a granitic suite from southern Germany (Siebel 1994). The slope of the isochron using whole rocks calculated to the time of emplacement of ~ 325 Ma indicates a pseudo-chron age of ~ 100 Ma (with a typical, almost ideal $\text{MSWD} = 1.4$), which is superimposed on the actual age. Because mixing between two different reservoirs on a whole rock scale is not a perfect process on a larger scale (kilometers), the correlation may exhibit an $\text{MSWD} > 1$ resulting in an errorchron relationship. Mixing may be identified in a 3-dimensional plot of $^{87}\text{Rb}/^{86}\text{Sr}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ [ppm] (Wendt 1993), as shown in Fig. 4b.

Isotopic Closure and “Cooling Ages”

Isotope dating requires all phases, whole rocks or minerals, to be in isotopic equilibrium at the time of formation. However, for large igneous bodies, cooling of magma and the mineral phases that crystallized from it do not occur instantly and contemporaneously. Because conductive heat transfer in igneous rocks is an inefficient process, the thermal gradient between the intrusive magma and the ambient rocks may persist for a long time, often for millions of years. Minerals in the igneous body

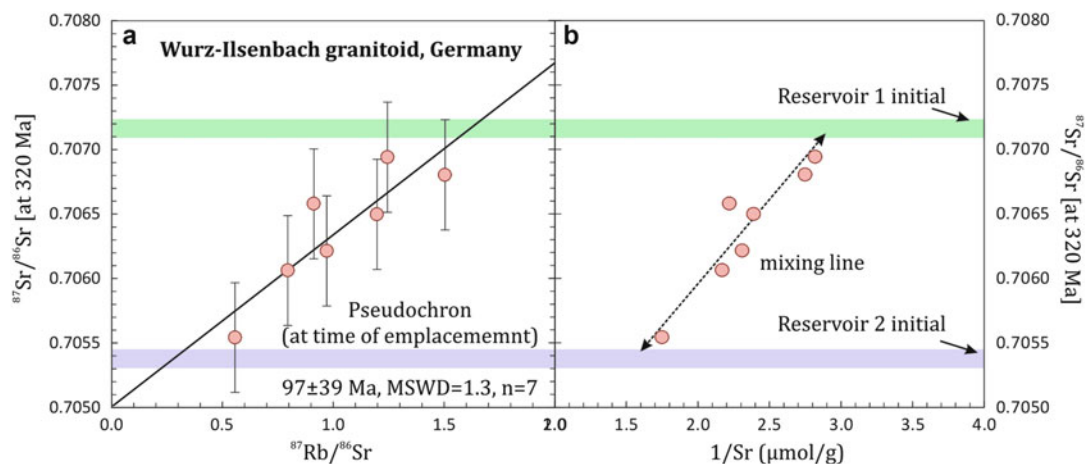


Fig. 4 (a) Pseudo-isochron produced by a two-component mixing between isotopically distinct reservoirs preserved in granites from Southern Germany (Data from Siebel 1994). The data are age corrected to the time of formation at 320 Ma, as deduced independently by $^{40}\text{Ar}/^{39}\text{Ar}$ isotope dating. (b) The reciprocals of the Sr concentration show a straight line correlation with isotopic composition that indicates mixing of two components with variable Sr concentrations (Wendt 1993). The combined pseudo-chron and isochron slopes yield an apparent, yet meaningless “age” of 423 ± 41 Ma ($MSWD = 1.7$; $n = 7$; (Siebel 1994)

remain open systems with exchange of parent–daughter isotopes by volume diffusion. Only when a certain temperature is reached are minerals considered “closed” for an isotope system. This temperature is called the closure temperature, T_C (Dodson 1973). Alternative scenarios are possible, in which a system is closed rather quickly after emplacement but is subject to interdiffusion of elements between minerals (Jenkin et al. 2001, 1995). For phases with high $^{87}\text{Rb}/^{86}\text{Sr}$, such as phengite, biotite, or K-feldspar, relative T_C has been empirically determined (e.g., Von Blanckenburg et al. 1989). They vary between 500 °C and 300 °C and may be dependent on grain size, chemistry, pressure, or fluid content (Villa 1998). The T_C for Rb–Sr is lower than for most other isotope systems including K–Ar or $^{40}\text{Ar}/^{39}\text{Ar}$. This effect has long been known (Armstrong et al. 1966; Delmoro et al. 1982; Verschure et al. 1980) and used to calculate cooling paths for igneous and metamorphic systems (e.g., Von Blanckenburg et al. 1989).

Rb–Sr analyses of different mineral phases can still yield coherent ages with a well-defined isochron relationship among different phases, even if all phases closed long after the actual emplacement event. This dates the time of cooling through isotope closure. Although initially considered a matter of grain size and diffusional processes (Dodson 1973), element exchange between coexisting phases may be equally important for Rb–Sr (Jenkin et al. 2001). Thus, Rb–Sr analyses of different grain fractions should not be used to determine cooling paths by Rb–Sr dating alone and are better accompanied by analyses of other phases with other isotope systems, which, in turn, have other closure temperatures. A cooling path may then be determined in a temperature–time diagram. Additional complications may, however, arise, due to diffusion below the T_C . Detailed micro-drill investigations (on a sub-crystal scale) in K-feldspar grains from a slowly cooled plutonic body indicate Sr isotope heterogeneity, likely induced by diffusion (Siebel et al. 2005), which can compromise bulk mineral analyses.

Timescales of isotope closure vary considerably and, as noted, depend on a number of parameters. A good example is cooling of the Great Dyke, a layered mafic intrusion in the Zimbabwe Craton. This massive mantle-derived igneous body is an extreme case of a magmatic body that intruded into presumably hot country rock, such that the thermal gradient between the intrusion and the ambient country rocks was small. Accordingly, the intrusion cooled very slowly, and reported Rb–Sr ages are

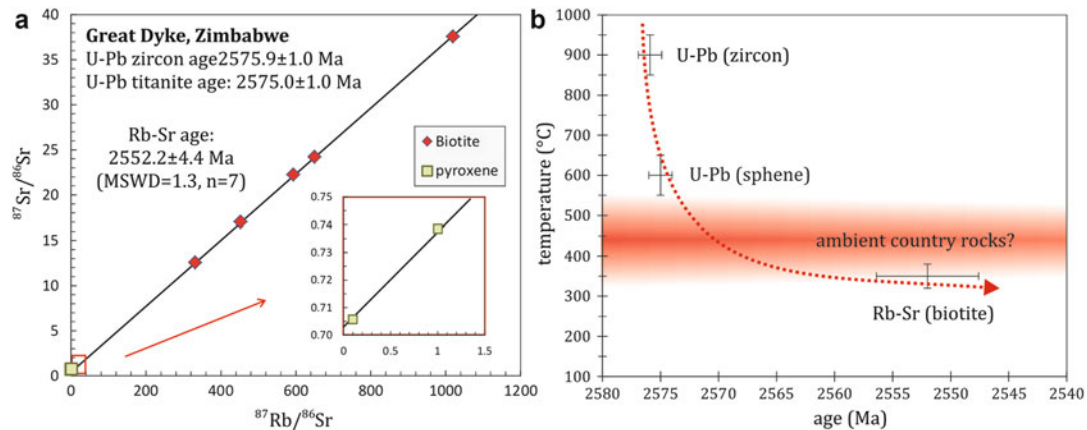


Fig. 5 (a) Rb–Sr age for the Great Dyke, Zimbabwe. (b) Cooling path of the intrusion by comparison with other chronometers (Modified after (Nebel and Mezger 2008))

~23 Myr younger than ages determined for the same rocks using systems with higher closure temperatures (e.g., U–Pb in zircon or sphene) (Nebel and Mezger 2008; Fig. 5). The age deduced from ortho- and clinopyroxenes is identical to the age calculated from combined pyroxene–biotite, which indicates a similar T_C for both minerals. Summing information from the available literature then allows a relative T_C for Rb–Sr that is phengite > K-fsp > biotite $\pm$ clinopyroxene.

Dating Metamorphic Rocks

For the dating of rocks, it is required that, after the time of its formation (termed t_0), a system remains undisturbed with respect to Rb–Sr systematics, i.e., that both Rb and Sr elemental and isotope abundances remain a closed system. That means that the amount of the parent nuclide Rb-87 must not be altered (by removal or addition) by exchange with the surrounding environment and that the daughter product Sr-87 must correspond to the amount of Rb responsible for the ingrowth. If a rock is subject to metamorphism, i.e., physical and/or chemical processes that lead to a change in its texture and mineralogical and/or chemical composition, this requirement may be compromised.

Metamorphic conditions can reach temperatures far exceeding T_C for Rb–Sr so that a system can “reset.” Metamorphism and the associated formation of minerals at the expense of existing ones often also include the release of fluids or involve fluids from outside the rock (metasomatism), which promote the diffusion of ions and/or the mobility of elements. This is especially the case for the classical “mobile” large ion lithophile elements (LILE) that include most alkali and alkaline earth elements (including Rb and Sr), and often the Rb and Sr budget in such rock associations can be significantly altered. Isotope systems are very sensitive to these processes, even without an apparent (i.e., visible) metamorphic overprint, and they may even affect a rock below the igneous T_C for an isotope system, e.g., because of dislocation effects in the crystal lattice that occur during the radioactive decay and isotope ingrowth, up to the point when a crystal becomes metamict. This susceptibility is often reflected in age relationships of old rocks that yield younger Rb–Sr ages than their presumed emplacement age (deduced from other chronometers) or no age information at all (isotope scatter that does not permit construction of an isochron). With the already relatively low T_C for Rb–Sr in most minerals (300–500 °C) compared to temperatures in metamorphic reactions that can easily exceed these values, this feature can have considerable impact on many rock assemblages

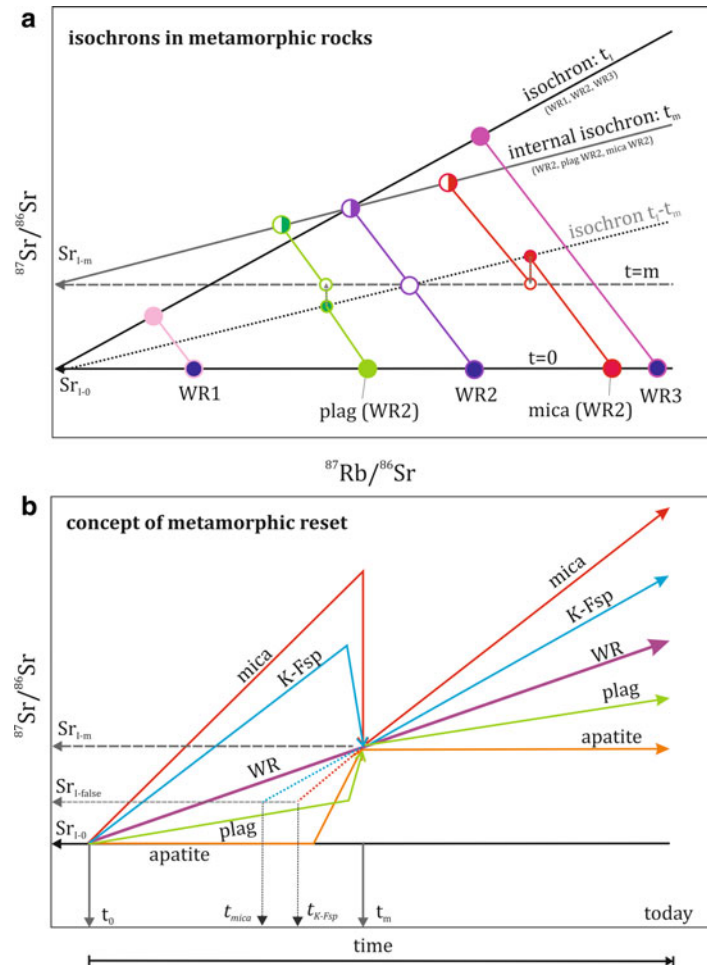


Fig. 6 (a, b) Modified after Faure (1986). (a) Concept of isotope resetting. Whole rocks 1, 2, and 3 preserve an isochron of the original igneous event with the age t_0 , whereas minerals of whole rock 2 give the metamorphic age t_m . Half-open symbols are metamorphic assemblages; open symbols are the reset assemblages of WR2 at the time t_m . At this time WR2 is internally homogenized with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of Sr_{I-m} . B: isotope evolution of various minerals of a whole rock during a metamorphic event. All phases evolve as a function of their $^{87}\text{Rb}/^{86}\text{Sr}$. At the time t_m , all phases are reunited and homogenized in their Sr isotope composition with a new initial Sr isotope composition Sr_{I-m} . The whole rock remains a closed system and is not affected by this event. Corrections of metamorphic phases to an incorrect age can yield false initials ($\text{Sr}_{I-\text{false}}$); reciprocally, an incorrect initial Sr isotope assumption will provide a biased model age (t_{mica} , $t_{\text{K-fsp}}$)

in old crustal terranes and has been a long-standing problem in Rb–Sr dating (Fairbairn et al. 1961; Riley and Compston 1962).

However, this seemingly strong limitation of the Rb–Sr chronometer can, in turn, be used advantageously to date “secondary events,” i.e., the time of metamorphic resetting, hereafter termed t_m . Internal mineral isochrons for individual whole rocks can yield age information on the thermal event, whereas on a whole rock scale the original emplacement age of an igneous rock can be preserved. For this to occur, the system is closed on a bulk rock scale and preserves its amount of accumulated Sr-87 and Rb concentration, and only a redistribution between mineral phases took place. This can be the case if little or no fluids are involved in the metamorphic reactions, as fluids often act as a transport medium for Rb and Sr beyond the scales of bulk rock samples. The combination of igneous whole rock and metamorphic mineral isochrons is illustrated in Fig. 6a, where whole rocks 1, 2, and 3 yield the original emplacement age (t_0), whereas the constituent

minerals of whole rock 2 in combination with the bulk rock yield the time of metamorphic reset (t_m). At t_m , minerals achieve isotope equilibrium with $^{87}\text{Sr}/^{86}\text{Sr}$ similar to that of their respective whole rock, and radiogenic ingrowth then starts anew as a function of the Rb–Sr in each mineral. This ideal case scenario of metamorphic reset on a mineral scale and preservation of primary age information on a whole rock scale has been observed in the Carn Chuinneag Intrusion in Scotland (Long 1964; Pidgeon and Johnson 1974). Unfortunately, in most cases the cooling of metamorphic terranes can be very slow such that individual mineral phases do not close contemporaneously, so that their isotopic clock does not start ticking at the same time. This is then reflected in an errorchron relationship that, at best, only allows the broad determination of cooling paths or an approximation of t_m that often fails modern requirements on precision.

The concept of isotope resetting is illustrated in Fig. 6b (redrawn after Faure (1986) and following the concept of Riley and Compston (1962)), where the isotopic evolution over time of different mineral phases with variable $^{87}\text{Rb}/^{86}\text{Sr}$ is shown. It is important to note that some phases reset earlier than others (or may solely be affected by the metamorphic events), all of which are a function of their individual metamorphic T_C (which as stated earlier can also include isotope diffusion) (Ganguly and Ruiz 1987). In most cases, Rb–Sr isotope systematics yield errorchron ages that may be geologically meaningless. However, in the worst case (often if only two or three data points are employed or they have a relatively small spread in $^{87}\text{Rb}/^{86}\text{Sr}$), Rb–Sr data do not allow distinctions between a true isochron or meaningless mixing age populations (Riley and Compston 1962). This can be the case if whole rocks are reset at different times or elemental and isotope exchange beyond whole rock scales occurred, but data coincidentally plot on a straight line within their analytical uncertainty. In the absence of other petrologic or isotopic parameters, the determination of model ages of, for example, K-feldspar and mica (t_{mica} , $t_{\text{K-fsp}}$) can assist in clarification of the geologic history of a sample, as, for a given initial Sr isotope composition, these ages should be identical. These model ages then should correspond to the correct igneous age. However, the initial $^{87}\text{Sr}/^{86}\text{Sr}$ for this calculation is often unknown, and iterative approaches by multiple phase analyses are often too imprecise to yield useful age information.

In many cases, one (or more) metamorphic event(s) results in a complete redistribution and homogenization of Rb–Sr systematics in all phases and on whole rock scales for very large metamorphic terranes. This has been shown by many early Rb–Sr studies on Archean metamorphic terranes in old cratons (e.g., Hurst et al. 1975; Kalsbeek 1981; Moorbath et al. 1977a, b). A complete reset is also possible during the metamorphic crystallization of sediments, so that metamorphic Rb–Sr ages t_m can be determined for para- and orthogneisses alike.

Obviously, without additional constraints it is not possible to predict to which extent isotopic exchange and homogenization occurred, and the possibility of isotope “inheritance” has been reported even for isotope systems with very high T_C , such as the Sm–Nd system (Roth et al. 2013). On the other hand, isotope systems with a high closure temperature may not yield metamorphic ages as they may only be partially reset, whereas Rb–Sr may have been fully re-equilibrated. Such a case is reported for the Yilgarn block in Western Australia (Fig. 7), where Rb–Sr systematics give a precise timing of metamorphic resetting (McCulloch et al. 1983). Sm–Nd data, however, preserved its isotope character during this metamorphic event and can be used to reconstruct the history of the precursor of the metamorphic terrane. Therefore, if placed in a geologic context, the Rb–Sr systematics of metamorphic rocks have the potential to yield precise and accurate age information and may otherwise simply be used to test the extent of isotope equilibrium (for a given age) by correction for radiogenic ingrowth to the respective initial ratios.

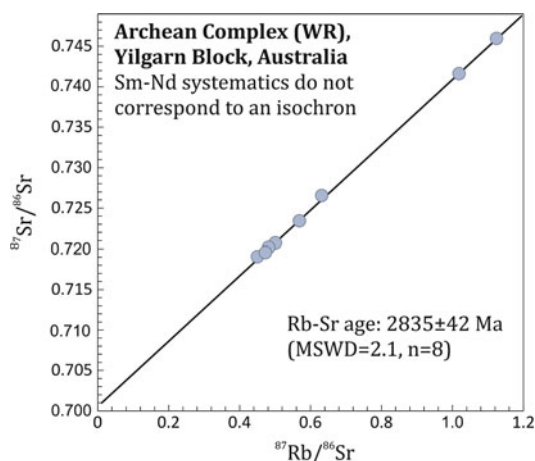


Fig. 7 Rb–Sr whole rock isochron for metamorphic gneisses from the Yilgarn Craton in Western Australia yields a precise metamorphic age, whereas Sm–Nd isotope systematics do not permit tight age constraints (2800 ± 150 Ma). When age corrected to the Rb–Sr age, the Nd isotope data is interpreted to reflect variable juvenile protoliths of the gneiss (McCulloch et al. 1983)

Dating Fluid Events and Ore Deposition

The fluid mobility of LILE implies that Rb and subsequently Sr can be mobilized in crustal fluids during low- to high-grade metamorphic events. Whereas this is often considered a problem for igneous rocks (they do not stay as a closed isotope system), there is a potential for dating such events with the Rb–Sr technique. In addition, mobilization of elements is often related to the formation of ores, and knowledge of the timing of ore formation is of great importance in economic geology or in regional geologic investigations. The Rb–Sr technique has long been exploited in dating base metal sulfide deposits, such as Mississippi Valley-type deposits (Brannon et al. 1992; Christensen et al. 1995; Nakai et al. 1990, 1993), which are associated with large-scale brine migrations under low temperatures (i.e., $<200^\circ\text{C}$; Nakai et al. 1993), or lode gold deposits that are either porphyritic or epithermal in nature (Yang and Zhou 2001). These ores often contain mineral assemblages with parent–daughter ratios that are unsuitable for dating, which makes age determinations of the mineralization notoriously difficult.

Sphalerite and pyrite are common sulfides formed during mineralization events and appear to contain a reasonable spread in Rb–Sr and enough material to obtain isotope results on mineral separates of reasonable size and quantity. This is of particular importance as sample heterogeneity (in $^{87}\text{Sr}/^{86}\text{Sr}$) can be significant (i.e., outside analytical reproducibility) in crystals that grow in the presence of fluids as fluid sources and compositions can vary in these systems. Hence, variations in $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ may occur between neighboring samples or within growth domains of single samples. In the latter case, full isotope equilibrium of all domains is required, which, under hydrothermal conditions, is not always the case. However, some fluid systems can be deposited on timescales of minutes (e.g., Weatherly and Hanley 2013) so that isotope equilibrium can likely be assumed in these systems.

An example of such an application is shown in Fig. 8 that shows pyrite-only isochrons for a lode gold deposit from China (Yang and Zhou 2001), where the spread in $^{87}\text{Rb}/^{86}\text{Sr}$ within individual crystals and/or batches of crystals is used as an advantage for dating. Pyrite separates from two individual veins yield two well-defined isochrons with a mean age of 125.2 ± 0.9 Ma. Both individual determinations give confidence that gold deposition from fluids in the veins occurred at

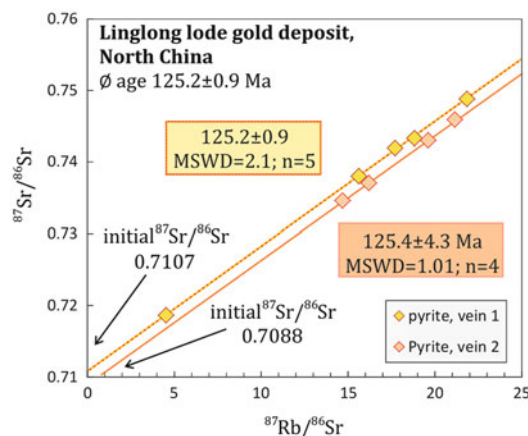


Fig. 8 Rb–Sr isochron for two individual veins from a gold deposit in China (Yang and Zhou 2001). Both isochrons indicate an identical age of deposition, yet display variations in their initial Sr isotope composition, indicative of distinct fluid sources. If combined, both veins would display an errorchron relationship

this time. However, as illustrated in the figure, the source of the fluids is distinguished by their initial isotope compositions, so that a joint-age determination would inevitably result in an errorchron.

Dating Extraterrestrial Material

The Rb–Sr technique was widely applied to meteorite and lunar research, predominantly in the 1970s and 1980s, with a wide number of applications (e.g., Allègre et al. 1975; Birck and Allègre 1978; Birck et al. 1975; Minster and Allègre 1976; Minster et al. 1982; Misawa et al. 1993; Nyquist et al. 1986; Papanastassiou and Wasserburg 1970; Papanastassiou et al. 1970; Shih et al. 1992). Even though extraterrestrial whole rock samples and mineral species have limited spread in $^{87}\text{Rb}/^{86}\text{Sr}$, their extreme age makes them suitable for dating with this technique. However, the use of Rb–Sr in cosmo-chronology has become less popular in recent years. The reason for this is the improvement in other dating methods and intense isotope tracing of reservoirs that has led to a much more refined chronology of early solar system events and the identification of multiple processes and events. This renders most whole rock dating approaches incorrect as they would lead to comparison of mixed populations of rocks producing geologically meaningless ages (Field and Raheim 1979). First analyses of a series of bulk meteorites yielded a good correlation among different groups of meteorites. Whereas absolute age determinations were hindered by the issue of decay constant uncertainties, these authors used the data to calculate an Rb decay constant of $1.402 \times 10^{-11} \text{ year}^{-1}$ (Minster et al. 1982), a value that is close to the recently refined value (Nebel et al. 2011; Rotenberg et al. 2012). However, it is now clear that, while this approach yielded important information at the time, replicate analyses using modern Rb–Sr methods would most certainly reveal isotope disequilibrium among these samples, as decades of meteorite research has revealed substantial isotope heterogeneity among early solar system reservoirs (cf. Hans et al. 2013).

A second serious problem for Rb–Sr dating of extraterrestrial samples is that of terrestrial alteration in most meteorites (if not reported as “falls”). Rb–Sr dating of such material should be accompanied by other chronometers, intense evaluation of trace element abundances that allow identification of primary igneous processes or secondary alteration, and/or careful treatment of samples (such as leaching). If these conditions are met, modern Rb–Sr dating can provide very precise and accurate information on the history of solar system material (Rankenburg et al. 2007). In

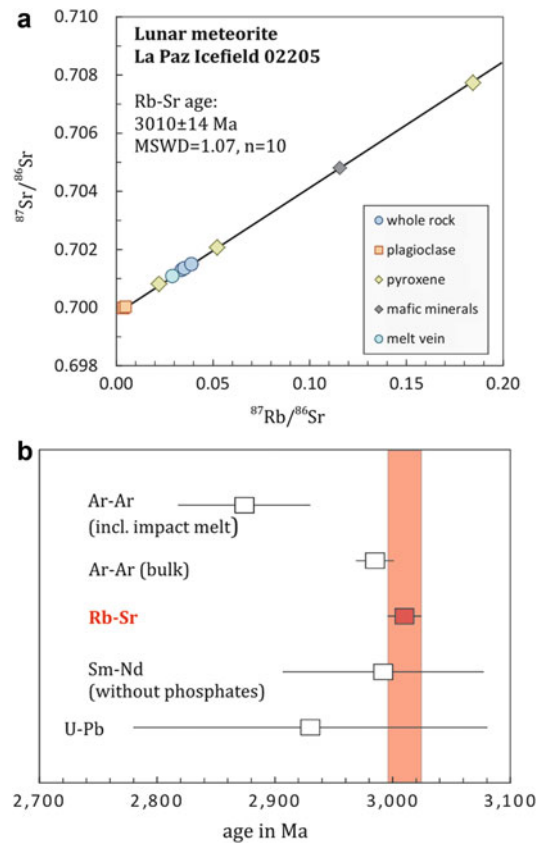


Fig. 9 Whole rock–mineral isochron (including a melt vein but excluding a leachate fraction) from lunar meteorite LAP02205 (Data taken from Rankenburg et al. (2007)). The Rb–Sr isochron yields an almost ideal MSWD of 1.07 indicating isotope equilibrium. **(b)** Comparison of the Rb–Sr age with other age data for the same meteorite; the Rb–Sr age is the most precise and likely indicates the time of formation of the rock. $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Fernandes et al. (2009)), Sm–Nd age (Rankenburg et al. (2007)), U–Pb age (Anand et al. (2006))

addition, if an isochron relationship can be established, the initial Sr isotope ratio of this isochron can provide invaluable information on the time-integrated evolution of the greater source domain, such as the Moon (Papanastassiou and Wasserburg 1970; Papanastassiou et al. 1970). In addition, despite the difference in age and origin for many meteorites, isotopic closure also applies to metamorphic events in space, and similar to terrestrial analogues, the Rb–Sr technique is capable of obtaining ages for high-temperature collision events, for example, on Mars (Nyquist et al. 1979), or meteorites that have been subject to metamorphic overprinting (e.g., Birck and Allègre 1978).

A good example of modern Rb–Sr dating of extraterrestrial material is the lunar meteorite La Paz Icefield 02205 (LAP02205). Rankenburg et al. (2007) analyzed bulk rocks, pyroxene, and feldspar separates (and additional phases) and obtained a Rb–Sr age of 3010 ± 14 Ma (illustrated in Fig. 9a). This age agrees with, but is more precise than, the corresponding U–Pb age of 2.93 ± 0.15 Ga (Anand et al. 2006) or the Sm–Nd age of 2992 ± 85 Ma (Rankenburg et al. 2007) on the same sample (Fig. 9b). The latter system has also been subject to disturbance in phosphates so that Rb–Sr appears to be more robust with respect to the nonsilicates that often occur in meteorites. Notably, $^{40}\text{Ar}/^{39}\text{Ar}$ results of 2985 ± 16 Ma and 2874 ± 56 Ma (Fernandes et al. 2009) on this meteorite appear to be somewhat younger, which at least in the first instance may be related to inaccuracies in the Ar decay constants (Begemann et al. 2001). Irrespective of the cause of difference in absolute

ages using various chronometers, it seems apparent that Rb–Sr can provide accurate and very precise age information that cannot otherwise be determined.

Conclusion

The Rb–Sr dating technique is a widely used technique in obtaining ages of igneous or metamorphic events and may be applied to dating volcanic sequences, ore deposition, or fluid-related events. In comparison with other dating techniques, there are several disadvantages, for example, its relatively low closure temperature and consequent susceptibility to isotope disturbance. However, if applied in a petrogenetic context or on samples that allow other means of identifying (hydro-)thermal overprints, it is a useful and reliable dating tool. In addition, it can also be used to date low-temperature events or the prolonged cooling history of igneous bodies or greater crustal terranes. The advent of modern analytical instrumentation now enables determination of high-precision Rb–Sr ages that are comparable in precision and accuracy with other dating techniques. Limitations such as poorly constrained thermal histories of samples and the necessity of species (mineral or rock) with a considerable spread in Rb–Sr ratios remain.

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Sedimentary Rocks (Rb-Sr Geochronology)

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Synonyms

Clay dating; Glauconite dating; Rb-Sr dating; Shale chronology; Sr dating; Sr geochronology

Definition

Application of the radioactive decay of ^{87}Rb to ^{87}Sr to determining the age of deposition of sedimentary rocks.

Characteristics

Absolute dating of sedimentary rocks is of interest to obtain depositional ages and to provide a quantitative link between the relative ages provided by fossil successions (biostratigraphy) and the geological time scale, and improve our understanding of the evolution of life through the fossil record. However, application of the Rb-Sr system to dating of sedimentary rocks has had variable results and has often proved to be problematic.

The Rb-Sr geochronological system is based on the beta decay of ^{87}Rb to ^{87}Sr with a half-life of 48.8 Ga, corresponding to a decay constant (λ) of $1.42 \times 10^{-11} \text{ a}^{-1}$, making the decay system potentially able to provide absolute age information for geological events throughout most of the Earth's history. The general decay formula for the Sr isotope system is

$$\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}_{(0)}} = \frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}_{(i)}} + \frac{{}^{87}\text{Rb}}{{}^{86}\text{Sr}} e^{\lambda t} - 1$$

where the subscripts (0) and (i) refer to the measured present-day and initial Sr isotope composition, respectively. Age determination with the Rb-Sr system typically involves construction of an isochron using minerals or rocks with as wide a range in Rb-Sr ratios as possible. Rb and Sr have chemical characteristics similar to K and Ca, respectively; therefore, Rb will tend to be concentrated in K-rich minerals and Sr will be concentrated in Ca-rich minerals. Examples of minerals in sedimentary systems with high-K contents and therefore high Rb-Sr are micas, alkali feldspar, and various clay minerals, whereas minerals such as carbonates and phosphates (e.g., calcite and apatite) are Ca-rich and therefore have low Rb-Sr. With time the ^{87}Rb in the minerals will decay to ^{87}Sr , such that high Rb-Sr minerals will become progressively more radiogenic (higher $^{87}\text{Sr}/^{86}\text{Sr}$) with time, whereas the amount of ingrowth of ^{87}Sr in the Rb-poor minerals will be

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lower or, in the case of Rb-free minerals, absent. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ of the different minerals or rocks phases will then define a line, an isochron, with a slope that is proportional to the age of the rock. The intersection of the isochron with the Y-axis, or alternatively analysis of a Rb-free phase or an assumption of an initial isotopic composition, provides the initial Sr isotopic composition of the system $^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$.

The age of the rock can then be calculated using the equation:

$$t = \frac{1}{\lambda} \ln(1 + \text{slope})$$

In order to obtain meaningful age information from an isochron, three fundamental assumptions must be fulfilled:

- (a) The minerals/rocks must have all formed in equilibrium with each other.
- (b) The minerals/rocks must have all formed from a reservoir of homogeneous isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$).
- (c) The minerals/rocks have been a closed system (i.e., not been subject to thermal or chemical disturbance) subsequent to formation.

There are three main groups of sedimentary rocks: clastic (transported), carbonate (biological), and chemical. Chemical sediments form by precipitation of minerals out of water (e.g., evaporates, carbonates, phosphates, and travertine in caves). Biological carbonate sediments (peat and coal are also biological) are formed from the accumulation of skeletal remains of organisms. The minerals formed in chemical sediments and in shells and skeletons are normally calcium-rich (e.g., calcite, apatite) and show a limited range in Rb-Sr. Thus, they are not suitable for Rb-Sr geochronology, although some can be dated using the U-series dating method, and will not be discussed further here. Siliciclastic sediments such as sandstones and mudstones form at relatively low temperatures at the Earth's surface as a consequence of erosion, transportation, and deposition of fragments and minerals from preexisting rocks dominated by silicate minerals. These sediments then undergo burial and diagenesis to become cemented into sedimentary rocks. Minerals that are unstable at surficial pressures and temperatures will tend to progressively break down during sedimentary processes to form new mineral phases, for example, feldspars will undergo hydrolysis to form clays (e.g., illite, smectite, kaolinite), many of which are K-rich and thus theoretically provide potential for dating using Rb-Sr.

The main difficulties encountered when applying the Rb-Sr system to dating of sedimentary rocks reflect uncertainties in the assumption that the sedimentary components had homogeneous isotopic compositions at the time of deposition and that the system has remained closed since. Most sandstones and clays consist of some mix of detrital phases and new authigenic minerals. Detrital minerals are derived from the eroding source region and have been transported unchanged or partially modified, and these grains will retain a Sr isotope signature reflecting the amount of ingrowth of ^{87}Sr from the decay of ^{87}Rb since their source region cooled through the closure temperature for the mineral in question. As the source regions for any particular region can comprise many different rock types of different ages and origins, this detrital component is potentially heterogeneous. Authigenic minerals grow during weathering, transport, or deposition and may therefore be in isotopic equilibrium with their transport medium (e.g., water). Because sedimentary processes take place at low temperatures, significantly below the closure temperatures for Sr isotope diffusion in the constituent minerals, the isotopic systematics are not reset to

equilibrium. Therefore, the fundamental assumption that all minerals in a sediment at the time of deposition or early diagenesis formed in equilibrium with each other and from a reservoir of homogenous isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}_{(i)}$) is unlikely to hold true.

Rb-Sr Dating of Clays

To avoid these complications, workers trying to date siliciclastic sediments have focused on fine-grained authigenic minerals such as clays that grow during deposition and early diagenesis and are so fine grained that they can equilibrate with the surrounding water. The assumption is then that these phases form in isotopic equilibrium and thus fulfill the criteria for creating an isochron. Subsequent variations in Sr isotopic composition in various clay fractions reflect their variations in Rb-Sr and ingrowth with time and can theoretically be used to construct an isochron. Two point isochrons may also be constructed if constraints on the initial Sr isotopic composition of the sediment can be made using the Sr isotope evolution curve for seawater, i.e. if an approximate age of the sediment is known beforehand or from analyses of interbedded carbonate or calcareous fossils.

Complications in the use of fine-grained clays for Rb-Sr geochronology exist because detrital components (including some clays) may be present even in the finest grain size fraction of sediments, and not all clays equilibrate with the surrounding water. Therefore, detailed X-ray diffraction studies of the clays are necessary to discriminate between detrital components and authigenic clays that have grown during diagenesis and low-temperature metamorphism. Furthermore, the ability of the clay minerals to equilibrate with the surrounding water also makes them susceptible to later disturbances by post-diagenetic interaction with pore waters which violates the remaining fundamental premise of isochron geochronology; that the minerals have remained a closed system since formation. It has also been shown that clay minerals can contain at least two different reservoirs of Sr with different origins and isotopic compositions, a loosely bound reservoir that can be released by leaching in acid or ammonium acetate and that represents the environment during deposition and clay crystallization, and a reservoir that is part of the crystal structure (e.g., Clauer et al. 1982).

The care and level of characterization that is required, and the complications involved, in obtaining geologically meaningful age data from clays in sediments are well illustrated in the study of Gorokhov et al. (1994). They separated the $<2\text{ }\mu\text{m}$ clay size fraction from a series of sediment samples from the Cambrian–Precambrian boundary in northern Estonia and Russia and then further separated these according to grain size. The samples were characterized by XRD to determine their illite crystallinity index by investigating the width of the (001) peak at half its height. A low index indicates a well-defined sharp peak and is indicative of well-crystallized illite which formed under relatively high-temperature conditions, whereas a high index indicates poorly ordered, less regular illite formed at lower temperatures (Dickin 2005). The clay fractions were then leached to produce 3-point isochrons (leachate, residue, and bulk) for each clay size fraction (Fig. 1).

The results from all clay samples and size fractions yielded a large scatter of ages but more importantly also revealed a trend of increasing age with increasing grain size (Fig. 2). In addition, the coarser-grained fractions were also characterized by XRD signatures that suggest crystallization at higher temperature, and thus, a significant detrital component was considered to be present in these fractions, subsequently resulting in older ages. Most of the other coarser-grained clay fractions were considered to be mixtures between detrital and authigenic components, and thus, the isochrons do not represent geologically meaningful ages but are instead mixing arrays. Nevertheless, when the data are combined in terms of grain size and crystallinity, some potentially

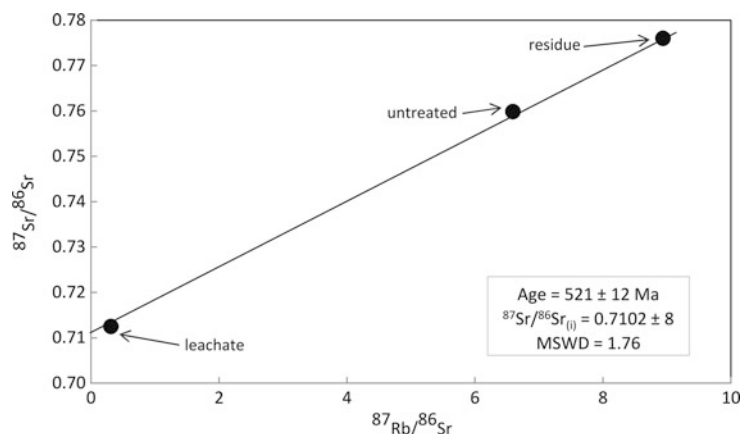


Fig. 1 Rb-Sr isochron for a representative clay sample from the Lontova claystones studied by Gorokhov et al. (1994) (sample 77NC80 < 0.1 μm fraction). Clays were leached with 1 N ammonium acetate, and a bulk sample, leachate, and residue were analyzed

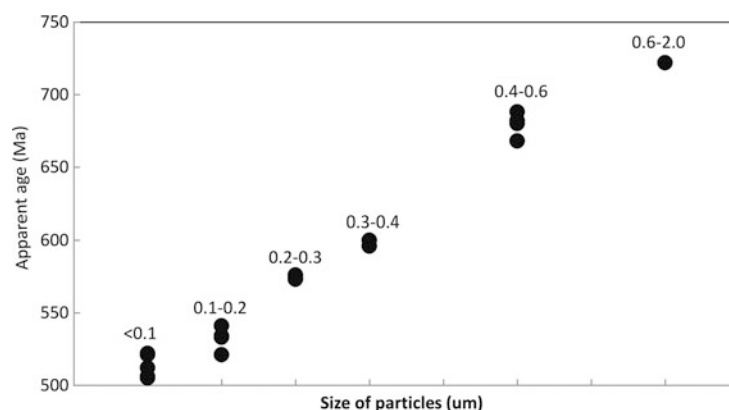


Fig. 2 Compilation of apparent Rb-Sr ages for clay fractions from the Lontova claystones (see Fig. 1) against size of the clay fraction analyzed, showing a clear positive correlation between grain size and age (From Gorokhov et al. (1994))

meaningful age information can be obtained. The well-crystallized fine-grained (<0.2 μm) clays define an isochron with an age of 533 ± 8 Ma which Gorokhov et al. (1994) estimate to be the best estimate of the age of sedimentation, whereas fine-grained disordered clays yielded a younger age (430–480 Ma) that may be related to later disturbance and interactions with subsurface waters.

Rb-Sr Dating of Glauconite

A more promising approach to dating sediments using both the Rb-Sr and K-Ar systems has been to analyze authigenic glauconite, a distinctive green to black K-Fe mica that is a member of the glaucony family of minerals and forms at the sediment–water interface in shallow marine environments characterized by low energy and low rate of deposition. Sediments with high abundances of glauconite are commonly called greensands due to the characteristic color of the mineral. Glauconite originates as a result of biological activity such as ingestion and excretion of sediments. These fecal pellets, composed primarily of clay as well as potential detrital and organic material, become progressively dissolved and recrystallized on the seafloor and during burial in a process termed glauconitization. In order for glauconite to be of use in either Rb-Sr or K-Ar geochronology, it must be first assumed that it formed in equilibrium with a homogeneous reservoir (e.g., seawater)

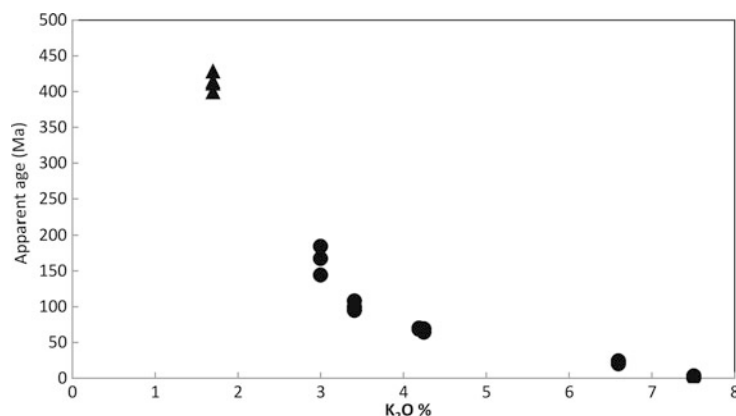


Fig. 3 Compilation of model Rb-Sr ages calculated assuming initial $^{87}\text{Sr}/^{86}\text{Sr}$ = modern seawater against K_2O content for glauconites (*circles*) and coexisting clays (*triangles*) from modern sediment samples. The variation indicates that glauconites with <7 wt% K_2O contain a significant component of Sr derived from detrital sources (From Clauer et al. (1992))

and has remained a closed system since. Detailed studies on modern glauconite have provided important insights into the glauconization process and show that it occurs as the result of a relatively slow, two-stage process (Clauer et al. 1992; Stille and Clauer 1994). Clauer et al. (1992) investigated modern glauconites from the Guinea and California coasts. The investigated samples were leached in acid prior to analysis to remove contaminants such as detrital clays and silicates, and carbonates. Sr isotope analyses of these leachates are similar to modern seawater and indicate that the source of this Sr is mostly marine. The isotopic compositions of the leached glauconites were then used to create 2-point isochrons, using the composition of modern seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$) as the initial composition. If there is no difference between the glauconite and seawater (i.e., an age of 0 Ma), then the glauconite is in equilibrium with seawater and could thus with burial and time yield meaningful geochronological information about the age of deposition. Strontium isotopic compositions of leached glauconite that are more radiogenic than seawater will result in positive present-day “ages” and suggest the presence of Sr in the glauconite inherited from detrital sources. These ages are of course geologically meaningless as the samples are effectively zero age. With burial and time, these rocks would develop isotopic compositions that would yield meaningless ages older than the age of deposition. Clauer et al. (1992) discovered a wide variation in apparent ages for the investigated glauconites and that the apparent age decreased with increasing K content, reaching a zero age at K contents in excess of 7 wt% (Fig. 3).

Clauer et al. (1992) therefore proposed that the initial stages of glauconite formation primarily involve recrystallization in equilibrium with progenitor materials and surrounding clays and are thus dominated by Sr inherited from the sedimentary source region. Isotopic analysis of these immature glauconites will not yield geologically meaningful ages. Later stages of glauconite growth are characterized by increasing K contents (>4 %) and involve chemical exchange with surrounding seawater. At equilibrium, this effectively resets the system to a homogeneous initial isotopic composition that is the same as that of the surrounding seawater. The glauconite then fulfills the first assumption of Rb-Sr geochronology as it formed from a homogeneous reservoir. With burial and isolation, it will begin to accumulate ^{87}Sr and thus potentially preserve the age of deposition and early diagenesis if there is sufficient spread in the Rb-Sr ratios of various glauconite fractions or when an assumed seawater composition or Rb-free phase such as apatite or calcite is used to constrain the initial composition. Careful chemical and mineralogical characterization of glauconite is therefore critical to ascertaining the validity of glauconite Rb-Sr ages.

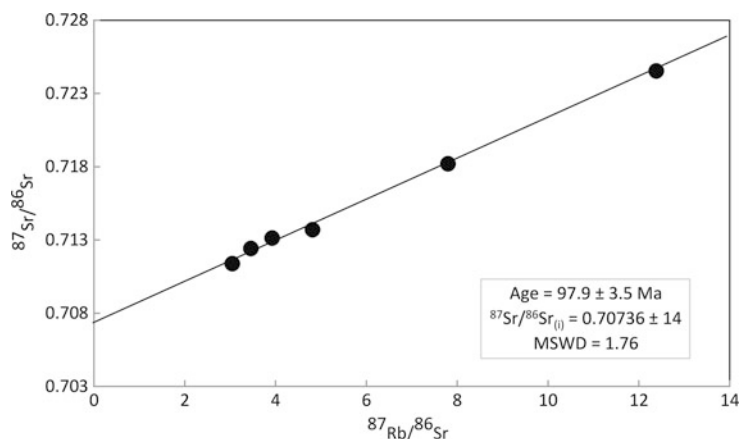


Fig. 4 Rb-Sr isochron for glauconites (*circles*) separated from sandstones and siltstones from southeastern France. K-Ar analyses on the same material yield an identical isochron age of 97.3 ± 0.4 Ma, and the age is interpreted as representing the time of deposition (From Rousset et al. (2004))

An example of successful Rb-Sr glauconite dating is given by Rousset et al. (2004). Several carefully separated, cleaned, and well-characterized fractions of glauconite from Cretaceous sediments in France were investigated. The glauconites have K_2O ranging from 6.1 to 7.4 wt% suggesting they are mature and well equilibrated based on the studies of Clauer et al. (1992) described above and yield enough variation in Rb-Sr to define an isochron with an age of 97.9 ± 3.5 Ma (Fig. 4). The initial Sr isotope ratio of 0.70736 calculated from the isochron is in agreement with the composition of seawater at that time and calcareous fossils from the same sedimentary succession. A K-Ar age on the same material that is identical within error confirms the validity of the Rb-Sr age and indicates that no post-depositional alteration or recrystallization affected the sediments as this would likely have affected the two isotope systems differently.

Conclusions

Dating the age of deposition or early diagenesis of sedimentary rocks is highly problematic, but in certain instances, meaningful depositional ages can be determined. The constituent minerals in most chemical and biological sediments do not have enough range in Rb-Sr to produce measurable differences in $^{87}\text{Sr}/^{86}\text{Sr}$ with time. Clastic rocks on the other hand comprise a mixture of detrital grains with variable isotopic compositions inherited from their source regions and authigenic minerals that grew during burial and therefore cannot be assumed to have been in isotopic equilibrium at the time of deposition. To avoid these problems, age information can be derived from Rb-Sr isotopic analyses of authigenic minerals such as clays and glauconite. However, such studies are complex and require careful characterization of the material prior to analysis in order to assess the robustness and significance of the geochronological results. In particular, for clay analysis, detailed mineralogical analyses are required to identify different generations of clays developed during various diagenetic and post-diagenetic processes and to avoid detrital minerals that may still be present in the fine-grained clay fraction. Studies of modern glauconites have shown that only mature glauconites with high K_2O contents appear to be in equilibrium with the surrounding seawater and thus fulfill the requirement of having formed from a homogeneous isotopic source.

Cross-References

- ▶ [Apatite](#)
- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Biostratigraphy](#)
- ▶ [Marine Carbonates \(U-Series\)](#)
- ▶ [Clays and Glauconites \(K-Ar/Ar-Ar\)](#)
- ▶ [Feldspar](#)
- ▶ [Geological Time Scale](#)
- ▶ [Mica](#)
- ▶ [Minerals \(Ar-Ar\)](#)

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Noble Gas Mass Spectrometer

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Noble gas mass spectrometry is a technique that allows for the measurement of isotopic ratios of small quantities of noble gases. Noble gases are typically extracted from samples in an extraction line, which connects directly to a mass spectrometer. Measurement of small quantities of gas is enabled by static-mode analysis, whereby gas is trapped in the mass spectrometer volume for the entirety of the measurement. Static mass spectrometric analyses were first considered by Aldrich and Nier (1948) and Nier (1981) and fully developed by Reynolds (1956).

Gas Extraction and Purification

Noble gas extraction and cleaning occur in an “extraction line” which has been pumped to ultrahigh vacuum (UHV) pressures of $<1 \times 10^{-9}$ mbar. Gas extraction from samples is typically achieved by furnace or laser heating. Gases thus released expand into the extraction line where they are purified to prevent isobaric interferences and source effects. Purification uses chemical traps (“getters”) made of metals that trap reactive gases and cryogenic traps, where regions of the line are held at temperatures below the vapor point of gases to be trapped. In some cases, different noble gases can be trapped and then later released for analysis, by varying the temperature of the cryogenic traps. Isotopic fractionation during extraction and purification is prevented by providing sufficient time for equilibration during gas expansions.

Mass Spectrometry

Purified noble gases are expanded into a mass spectrometer volume, which has typically been pumped to UHV until just prior to the inlet time. After allowing for isotopic equilibrium, the inlet valve is closed and analysis is initiated. Noble gas mass spectrometers contain a Nier-type electron impact ion source, which relies on a hot filament to create a beam of electrons that collide with and ionize gas atoms in the source. Ionized atoms are accelerated and analyzed as described in the entry on mass spectrometry elsewhere in this volume.

The isotopic composition of gas in the mass spectrometer evolves over the course of a measurement, due both to gas consumption and to outgassing from the walls of the mass spectrometer. Thus, each isotope is measured over a period of time, and the resultant data evolutions are fit with a line or curve that is extrapolated back to the time when gas was first expanded into the mass spectrometer. These “time-zero” fits for each isotope are assumed to represent the relative isotopic abundances of the samples.

Data must be corrected for background contamination and isotopic fractionation. Background corrections are made by replicating run conditions without heating the sample. Often blanks are run interspersed with samples, and a long-term fit of blank values is used to correct data. Isotopic

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fractionation, or discrimination, is corrected via the measurement of a gas with a known isotopic ratio; for Ar this is most commonly the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ value.

Geochronometers that rely on noble gas mass spectrometry include $^{40}\text{Ar}/^{39}\text{Ar}$, (U–Th)/He, $^4\text{He}/^3\text{He}$, tritium (by ^3He ingrowth), and cosmogenic radionuclides.

Cross-References

- ▶ [\$^4\text{He}/^3\text{He}\$ Dating](#)
- ▶ [Ar–Ar and K–Ar Dating](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Minerals \(Ar–Ar\)](#)
- ▶ [U–Th:He Dating](#)

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Amino Acid Racemization, Biostratigraphy

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Definition

Amino acid racemization biostratigraphy refers to using the ratio of right-handed (D) to left-handed (L) amino acids (D/L value) preserved in sediment or fossils to determine the age of sedimentary deposits including the duration of time recorded in sedimentary deposits. This can be done by direct comparison of D/L values to determine relative ages or by using calibrated D/L values to estimate ages in calendar years.

Characteristics

The age of sedimentary deposits is of fundamental importance to many topics in stratigraphy, sedimentology, evolutionary biology, and paleobiology. Amino acid racemization (AAR) provides a cost-effective way to directly date large numbers of fossils, and it has revolutionized the way paleontologists have been able to study the age of fossil deposits. AAR has made three key contributions to biostratigraphy. (1) AAR D/L values are one of many methods used to determine the relative age of sedimentary deposits (older deposits have higher D/L values). (2) AAR data are one of a few methods used to quantify the extent of mixing in sedimentary deposits. (3) Calibrated AAR data have enabled cost-effective studies of time-averaging (the amount of time recorded in a single deposit).

The use of AAR in biostratigraphy dates back to the 1960s (e.g., Hare and Mitterer 1967) and took hold in the 1970s (e.g., Bada et al. 1970; Bada and Protsch 1973). Because the rate of racemization increases with increasing temperature, the timespan over which AAR is useful depends on climactic conditions. AAR is useful over longer timespans in colder climates, stretching back over a million years in areas such as New Zealand (Bowen et al. 1998, and see ► [Amino Acid Racemization, Coastal Sediments](#)).

Post-deposition mixing and other factors impose fundamental limits on the resolution of fossil records. While D/L ratios can be used to demonstrate that two sediment layers have distinct age distributions (i.e., that one deposit is older than another), calibrated AAR enables the amount of time within a deposit and between deposits to be quantified. Calibrated AAR has been widely and primarily used to study sediment mixing processes in Holocene-aged sediments (e.g., Meldahl et al. 1997; Kowalewski et al. 1998, 2000; Carroll et al. 2003; Kidwell et al. 2005; Barbour-Wood et al. 2006; Kosnik et al. 2007, 2009, 2013; Krause et al. 2010; Simonson et al. 2013). The use of AAR as a cost-effective means of dating large numbers of shells has enabled these studies to date multiple shells per sedimentary deposit and quantify the amount of time recorded rather than

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relying on a single age estimate. These datasets have enabled others to test mechanistic models of sediment mixing and fossil assemblage formation (e.g., Olszewski 2004).

In other cases, AAR has been used for recognition of taphonomic processes, such as shell preservation and transport (Murray-Wallace and Belperio 1994; Wehmiller et al. 1995; Martin et al. 1996). In these latter studies, it is often observed that samples of one or more Pleistocene-aged specimens can be found mixed into Holocene shell accumulations and that the source units for these reworked Pleistocene samples can also be identified in the region using AAR (Wehmiller et al. 1995; Martin et al. 1996).

A key advantage of AAR when dating fossil deposits, relative to other methods such as Pb-210 or OSL, is that AAR directly dates the fossils rather than the surrounding sediments. Directly dating the fossils avoids any biases associated with differential sediment mixing.

Cross-References

- ▶ [Amino Acid Racemization Dating](#)
- ▶ [Amino Acid Racemization, Coastal Sediments](#)

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Luminescence, Earthquake, and Tectonic Activity

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Definition

- *Paleoearthquake*

An old, often prehistoric, earthquake.

- *Paleoseismology*

The study of paleoearthquakes, especially their geological expression, location, timing, and size.

- *Recurrence interval*

The repeat time of major earthquakes.

- *Slip rate*

The average velocity with which one side of the fault moves with respect to the other.

- *Earthquake catalogue*

A comprehensive earthquake database.

Introduction

On average, 15 earthquakes with a magnitude of 7 or greater occur on earth every year. Because of their devastating potential, much effort has been devoted to finding a reliable method for predicting the location and time of large earthquakes. So far these efforts have been unsuccessful. However, if the recurrence intervals for earthquakes of various magnitudes in the region of interest were known, it is possible to estimate the probability of an event in the future. Therefore, determining the average rate of recurrence of strong earthquakes on a fault is a key element in long-term hazard assessment.

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Seismic Hazard Assessment

Seismic hazard assessment (see Kijko 2011) is based mainly on analysis of seismicity and knowledge of past earthquake activity in a region. Past earthquake records come in three categories: instrumental, historical, and prehistoric. Instrumental data (post 1890s) cover a too short period, and historical records are also short compared to the repeat times of large earthquakes on a fault. In most parts of the world, even in parts of old countries such as China, Japan, Iran, and the Mediterranean regions, historical information reaches back a maximum of a few thousands of years. However, the recurrence interval of large earthquakes on many important faults is several thousands of years (e.g., 7 ka in Xiyangfang, China (Yanchou et al. 2002); 3 ka in NE Iran (Fattahi et al. 2006)). Therefore, analysis of paleoearthquakes is required to complete the catalogue of earthquakes.

Fortunately, geologic sedimentary strata and geomorphic features preserve evidence of tectonic deformation and landscape changes caused by large earthquakes at or near the earth's surface. Geology and geomorphology identify and evaluate the location and extent of past fault displacements near surface folding and features related to coseismic deformation. Luminescence dating methods, among other geochronology techniques, determine the timing of these types of deformation. Paleoseismology uses these records to understand the faulting process (McCalpin 2009). The majority of paleoseismic studies have been undertaken to provide input for seismic hazard assessments (e.g., Gurpinar 2005). Paleoseismic data have been used for producing probabilistic seismic hazard maps (see Kijko 2011) which include information on fault location, geometry, dimensions, slip rates, and recurrence intervals (see Kijko 2011).

Recurrence Interval, Slip Rate, and Active Fault

There are two ways to estimate recurrence intervals. One method is direct dating of evidence of paleoearthquakes. The second method is to divide the average displacement per event by the long-term slip rate of the fault. Long-term average slip rate is calculated by dividing the cumulative displacement (net slip required to produce the observed deformation across the fault) by the total time over which this displacement occurred (the age of the deformation).

The deformation can be horizontal deformation of a geomorphic or man-made feature such as river or road or the vertical deformation of dated strata in the subsurface or geomorphic surfaces overlying the blind thrust (monoclines, anticlines). The vertical slip rate, the net slip rate, and the dip of the blind fault are trigonometrically related to each other. Therefore, if vertical slip rate and dip are known, the net slip rate can be calculated.

Slip rate is a key to understanding the relative importance of active faults in an area and the hazard those active faults present to local residents and developments. There are different definitions for "active fault" based on geologic or engineering purposes in different countries. However, a fault is commonly considered to be active if it has moved at least once, up to a certain time in the past, such as the last 10 ka, 35 ka, 50 ka, or 1.8 million years ago (e.g., Lee et al. 2006; USGS website <http://earthquake.usgs.gov/learn/glossary/term=activefault>). An active fault exhibits offsets and can therefore be identified by recognizing and dating tectonically deformed surface or material. Active faults, faulted land forms, and coseismic surface ruptures can be identified by different methods, including satellite images, aerial photographs (e.g., Lin et al. 2006; Fattahi et al. 2007), various geophysical techniques, airborne light detection and ranging (LIDAR), airborne laser swath, mapping, and field surveys (see Kijko 2011).

Evidence for Prehistoric Earthquakes

Earlier classifications of paleoseismic evidence are modified to 16 categories and 3 levels as primary or secondary, on-fault or off-fault, and stratigraphic or geomorphic (McCalpin 2009, Table 1.2). Primary evidence is formed by tectonic deformation and reflects seismic surface faulting or folding, whereas secondary evidence is produced by earthquake shaking or is a response to strong ground shaking. These evidences are either above a fault trace or away from a fault trace and are coseismic or postseismic features, which are preserved as stratigraphic or geomorphic evidence. This distinction often determines how to approach paleoseismic field investigations. The geomorphic method usually measures and dates the amount of landform deformation during paleoearthquakes. Fault scarps, fissures, folds, colluvial aprons, tilted surfaces, uplifted/subsided shorelines, and tectonic alluvial terraces are typical examples of primary geomorphic evidence. Landslides, sand blows, and rockfalls are examples of secondary paleoseismic geomorphic evidence.

The stratigraphic method usually measures and dates deformed strata in exposures (McCalpin 2009). Examples of stratigraphic paleoseismic evidences can be divided into primary and secondary evidence. Primary evidence include displaced or folded strata, unconformities, scarp-derived colluvial wedges, tsunami deposits, zones of sheared sediment, fissures, and uplifted, subsided, or tilted surfaces located some distance from the fault. Secondary evidence includes, for instance, sand dikes and other liquefaction features, filled craters, soft-sediment deformation structures, and turbidity current deposits.

Evidence of paleoearthquakes and old surface ruptures are often minimal directly on the earth's surface. Therefore, trenches are excavated to expose faults and young strata that record the evidence. In outcrops or trenches, corresponding stratigraphic evidence can be found. A trench log is used for defining and mapping the sequence of deformation, sedimentation, and weathering exposed at a site and for recording evidence of surface-rupturing earthquakes. These records (see Toda 2011, Fig. 4) can be preserved as direct fault exposure, such as upward fault termination, fissure fill, scarp-derived colluvial wedge, wrapping, folding, minor fracturing, and inferred offset, each of which is defined as an “event indicator” (see Toda 2011). Luminescence dosimeter minerals (quartz and feldspar) inside these event indicators are used to find the age of paleoearthquakes.

Luminescence Dating of Prehistoric Earthquakes and Faulting

Luminescence dating of earthquake-related deposits offers great potential for dating evidence of past earthquakes and faulting for a number of reasons (see Fattahi 2009). Daylight or friction temperature can reset the luminescence “clock” of sediments before burial due to earthquakes. Therefore, luminescence dating techniques can be applied for age determination of any of paleoearthquake evidence if the clock of quartz or feldspar inside that evidence is reset during, or just prior to, paleoearthquakes. They constrain timing of paleoearthquakes directly or indirectly by calculating ages of deformed stratigraphic units and underlying or overlying undeformed strata.

The most direct techniques for dating active faults and paleoearthquakes are dating fault scarp, fault-scarp colluvium, fault gouge, or liquefaction features such as injection dike and sand blows (deposition from the surface rupture of an injection dike). Although these techniques directly date the formation of coseismic features, age uncertainties can be relatively large.

Indirect dating methods involve bracketing the age of the paleoearthquake by luminescence dating of structures or deposits that predate and postdate the paleoseismic evidence. Maximum

ages are obtained from sediment deposited before the paleoearthquake. Minimum ages are obtained on material younger than the earthquake. The accuracy and precision of luminescence dating may be high, but the ages themselves may not provide close constraints on the age of faulting.

Fault-scarp and fault-collapse wedges have been identified as the most important records of the paleoearthquakes (Allen 1986). Fault-collapse wedges are a kind of colluvial deposit of sediments formed as wedge-shaped deposits on the foot slope. Colluvium is a term that describes sediments that are eroded from and transported along hill slopes by gravity. Reverse and normal faulting chronologies can be reconstructed from luminescence ages on fault-scarp colluvial wedge sediments (e.g., Fattahi et al. 2006; Porat et al. 2008). Colluvial wedges and fault planes are identified from exposures and trenches, while materials from buried soils within the faulted sediments are dated to obtain a fault-rupture chronology. A suitable exposure or trench exhibits multiple faulting events with clear displacements and consequent colluviation. For reverse faulting, the approach assumes that an overhanging fault scarp is produced coseismically and immediately following the earthquake, hanging-wall collapse to form an angle-of-repose debris slope. On the assumption that the production process of colluvial wedge is sufficiently slow for the sediments to have been exposed to sunlight long enough to reset the luminescence clock, direct dating of discrete fault-rupture events can be achieved by OSL dating of fault-scarp colluvium. For normal faulting, a vertical throw of some meters is not uncommon for the surface expression of faulting. Immediately following the earthquake, there would be a contour step, the low side of which would then become progressively filled with sediment. Normal faulting chronologies can be reconstructed from luminescence ages on colluvial wedge, slope-wash sediments, sag-pond deposit, and the soil horizons that underlie and overlie the wedge. The age of the event horizon decreases away from the fault due to the time taken for soil to pour laterally, accreting scarp-derived colluvium. The age of the event horizon might also be extrapolated from the age of several subsamples of the buried soil horizon. Luminescence surface-exposure dating recently introduced by Sohbati et al. (2012) theoretically has the potential to date fault scarp directly.

The usual approach to dating individual paleoearthquakes on strike-slip faults is to bracket the earthquake by dating the youngest datable stratum deformed by the quake and the oldest datable stratum that overlies the earthquake horizon (McCalpin 2009). However, for strike-slip fault, direct luminescence dating of a fissure fill can provide the age of the faulting event (e.g., Fattahi et al. 2010).

Fault gouge is formed by brittle fracturing of rocks as a result of slip along the faults during an earthquake. Luminescence dating of gouge to date neotectonic movements and past seismic events is based on the assumption that during the faulting event, the luminescence intensity of the gouge material is “zeroed” by either frictional heating or mechanical deformation or a combination of these. Even with agreement between TL and radiocarbon ages and despite consistent TL and IRSL data, there has been debate about the resetting of the luminescence signal in fault gouge. Some researchers propose a grain-size dependence with finest grains almost certainly reset, while others revealed no evidence for resetting of fault gouge (see Spencer et al. 2012 and references there in). It is suggested that luminescence emission from fault gouge samples has the potential to determine the age distribution of distinct deformation microstructures (Spencer et al. 2012). Such age determination could help constrain some of the proposed micromechanical models for shear localization in fault gouge, for example, identifying the relative effect of stress-driven mass transfer processes.

Injection dikes correspond to episodic pulses of an increasing hydraulic pressure generated mostly by seismic loading during earthquakes. These injection dikes (formed by liquefaction

during earthquakes) were used for reconstruction of paleo-epicenter locations (McCalpin 1996 and references therein) and have been under investigation to be dated by OSL in an attempt to directly date seismic events (e.g., Thomas et al. 2007).

Sand blows are lenticular sand bodies that were erupted onto paleo-ground surfaces and were fed by sand-filled dikes that were sourced from subjacent liquefied sand beds. Age constraint on the timing of liquefaction and seismic activity may be obtained by OSL dating of sand blows formed by the surface rupture of liquefaction features and injection dikes (e.g., Thomas et al. 2007).

Dating tsunami events is important in estimating the recurrence intervals of catastrophic events and hazard risk assessment. OSL measures the times elapsed since sedimentation, so direct dating of tsunamigenic sediments by luminescence is possible if signal resetting is complete. Usually, aeolian and fluvial resetting of the luminescence signal takes place during sediment transport. However, the process of sediment transport by tsunami is often rapid: maximum tens of minutes for each half wave with total sedimentation lasting several hours. The flow may be too muddy to expose all sediments to light and the tsunami may occur at night. Consequently, only limited resetting occurs during transport. The assumption for zeroed luminescence signals in tsunami-deposited sediments is that the source sediments are well bleached prior to tsunami entrainment. The source material is sediment from the coastal and near-shore zone that is constantly reworked by waves and tides. Intertidal sediments from various locations and beach-face sediments deposited by a combination of wind and wave action have been shown to have a near-zero residual luminescence signal. OSL dating of deposits of the 2004 Indian Ocean tsunami and paleotsunami sediments of known age proved the general applicability of the method for tsunamigenic sand sheets (see Brill et al. 2012; Prendergast et al. 2012 and references therein).

Luminescence Dating of Tectonic Movements

Terraces, alluvial fans, fluvial, and dry lake deposits are datable by OSL and can be important records of tectonic activity. Fault activity or fold deformation can uplift or subside land and change channel patterns near known structures (e.g., Thamó-Bozsó et al. 2010). Land uplift can block a river and make a lake or change the direction of rivers. River and marine terraces can be dated by OSL to determine the rate of uplift (e.g., Choi et al. 2003). Thick basin-fill sediments can be dated to determine subsidence rates (e.g., Chen et al. 2003). Late Quaternary landforms which are displaced by a fault can be used to determine the slip rate and average recurrence interval (e.g., Fattahi et al. 2007). OSL can provide dates of deformed and undeformed fluvial and aeolian sequences which can be used to find the timing of neotectonic activity (e.g., Thamó-Bozsó et al. 2010). IRSL dating of the inland fans/terminal fans (as the potential geomorphic markers) can be used to determine the shift of neotectonic activities in a region (Pati et al. 2012).

Luminescence dating has been used to assess tectonic activity by studying the fluvial geomorphic response of rivers to deformation (e.g., Rittenour 2008 and references therein). These include:

- Determining the timing of the switch from a highly sinuous channel to a straightened channel as a response to periodic clustering of seismic events and decreased gradient due to fault displacement
- Fold migration during the Holocene era due to fault length extension
- Examining the faulting and uplift history along a river and comparing the influence of tectonic uplift and climate for the formation of strath terraces
- Rates of active faulting during the late Quaternary fluvial terrace formation at a river

Conclusion

Luminescence dating is rapidly evolving into a very powerful tool for determining the depositional age of earthquake-related sediments. It can do this because of its versatility in directly sampling targeted features and deposits using the most common minerals on the earth: quartz and feldspar. Following the successful application of TL dating for paleoseismic reconstruction (reviewed by Fattahi 2009), a new approach using OSL was employed to date paleoearthquakes and related sediments that have been displaced and exposed to daylight by any physical phenomena associated with an earthquake (e.g., ground motion, ground failure, surface ruptures, liquefaction, and tsunami). These dates are also essential for estimating the activity of earthquake faults, understanding neotectonic processes and rates, determining fault slip rates, and establishing recurrence intervals of fault activities. These are only the most prominent uses.

Luminescence dating results can be used not only to resolve paleoseismological problems on their own but also to prove if a fault is active for engineering purposes. Ages of paleoearthquake features plus all possible background information (geomorphology, structural geology, sedimentology, various geophysical records, results from other investigations, etc.) make paleoseismological interpretation of the results possible, which provide useful new insights and information for earthquake hazard risk assessment.

Cross-References

- ▶ [Luminescence Dating](#)
- ▶ [Luminescence, Coastal Sediments](#)
- ▶ [Luminescence, Colluvial Sediments](#)
- ▶ [Luminescence, Fluvial Sediments](#)
- ▶ [Luminescence, Geomorphological Processes](#)
- ▶ [Tsunamigenic Sediments](#)

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Luminescence Dating, Instrumentation

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Definition

The basic instrumentation required to obtain a dose based on optically stimulated luminescence (OSL) signals consists of four main components: (i) a luminescence detection system, (ii) a stimulation light source, (iii) a heating system, and (iv) an irradiation facility. To obtain a thermoluminescence (TL) dose, a stimulation light source is not required.

Introduction

Luminescence dating is an absolute chronological technique widely used in archaeological and geological dating but also with applications in other areas of retrospective dosimetry such as environmental, accidental, medical, and forensic dosimetry. In dating applications an age is determined by measuring the dose absorbed by the target mineral, primarily quartz and feldspars, and dividing it by an independently determined dose rate in the media. This dose rate is mainly derived from the flux of ionizing radiation emitted from naturally occurring isotopes (from the thorium and uranium series as well as potassium-40) and from cosmic rays and is determined using methods such as gamma spectrometry, beta counting, alpha counting, inductively coupled plasma-mass spectrometry (ICP-MS), and neutron activation analysis. These measurement techniques and the associated instrumentation are described elsewhere. Here, the main emphasis is placed on the instrumentation required to determine the dose absorbed by the target mineral using luminescence techniques.

Luminescence Detection System

Many natural phosphors are only weakly luminescent making good light collection important. This requires a sensitive photon detector with a low noise (background) level to obtain a good signal-to-noise ratio. Luminescence is emitted in all directions, but the use of reflective metal sample holders helps to maximize the light emitted toward the detector. The distance between the photon detector and the sample should be as short as possible, since only a small increase in this distance will lead to a considerable loss in light collection efficiency. Alternatively, suitable optics can be used to improve the light detection.

The light detection system consists of two components: (i) a photon detector and (ii) detection filters.

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Photon Detector

The most commonly used photon detector in luminescence dating is the photomultiplier tube (PMT), which converts photons into cascades of electrons. The quantum efficiency of PMTs is typically up to ~30 % (number of electron pulses per photon crossing the detection area) depending on the wavelength of the incident light. The bialkali EMI 9235QB PMT is widely used; this has a quantum efficiency of 25–30 % in the range from ~200 to ~450 nm making it suitable for detection of UV/blue luminescence from both quartz and feldspar (emitting mainly in the range 350–450 nm, e.g., Huntley et al. 1991). PMTs with an extended sensitivity in the red region (e.g., R943-02 Hamamatsu GaAs tube) are also used for red TL measurements of quartz and feldspar (e.g., Vandenberghe et al. 2009; Fattahi and Stokes 2000; Jain et al. 2005) or for IR-RF dating of feldspars (e.g., Krbetschek et al. 2000; Buylaert et al. 2012). Such PMTs need to be cooled to ~ -10 °C to reduce dark count.

PMTs do not provide any information on spatial variation of the emitted luminescence. Various imaging systems have been developed (see summary in Bøtter-Jensen et al. 2003) including the use of charged coupled devices (CCD). Recently, the use of EMCCD cameras has been suggested (Clark-Balzan and Schwenninger 2012; Richter et al. 2013).

Detection Filters

The main function of the detection filters is to define the spectral detection window, but they must also shield the photon detector from scattered stimulation light. The intensity of the emitted luminescence is $<10^{-15}$ times the intensity of the stimulation light, so for most applications it is very important to ensure that the spectral stimulation and detection windows are well separated. UV emissions (e.g., quartz, with stimulation with blue 470 nm light) are commonly detected through the broad band Hoya U340 glass filter, which has a peak transmission at 340 nm (full width at half maximum (FWHM) 80 nm). Blue emissions (e.g., feldspar, with stimulation with IR 870 nm light) are typically measured using a combination of BG3/Schott 7–59 and BG 39 glass filters, which has a peak transmission at ~380 nm (FWHM ~60 nm). This filter combination is also widely used for TL measurements, usually with the addition of heat-absorbing filters to reduce the contribution from blackbody radiation.

Stimulation Light Sources

In OSL, optical stimulation results in the eviction of trapped charge; subsequent recombination may lead to the emission of a luminescence signal. The probability of eviction and hence the luminescence signal intensity depends on the photoionization cross section of the target trap(s). This cross section is dependent on both the wavelength and the intensity (effective stimulation power) of the optical stimulation. In general, a brighter luminescence signal is obtained as the wavelength is decreased and the stimulation power is increased. Optical stimulation is usually achieved using a constant light intensity (CW mode), but the intensity can also be modulated to give a better visual insight into the number of traps contributing to the OSL signal (e.g., linearly modulated OSL, LM-OSL; Bulur 1996). In both CW and LM modes, the luminescence is recorded during stimulation. In pulsed OSL (POSL, e.g., McKeever et al. 1996; Denby et al. 2006), the stimulation light is pulsed and the OSL is measured between pulses. In luminescence dating applications, POSL is mainly used to separate quartz and feldspar OSL signals instrumentally (e.g., Thomsen et al. 2008) and in combination with time-resolved detection to obtain insight into luminescence recombination processes (e.g., Jain and Ankjærsgaard 2011).

Optical stimulation is often achieved using inexpensive and compact arrays of individual light-emitting diodes (LEDs, e.g., Bøtter-Jensen et al. 2010), which can be easily intensity modulated and can have a stable light output. A disadvantage of LED stimulation is the relatively broad emission (half width $\sim 20\text{--}30$ nm) with significant tails. Thus, additional cutoff filters are often required to obtain sufficient spectral separation of stimulation and detection windows (Bøtter-Jensen et al. 1999).

Nevertheless, optical stimulation can be achieved using any optical stimulation source, e.g., filtered lamp systems (Bøtter-Jensen and Duller 1992), lasers (Huntley et al. 1985; Duller et al. 1999; Richter et al. 2013), and laser diodes (Bøtter-Jensen et al. 2000; Richter et al. 2013). One advantage of using a laser-based stimulation source is the monochromatic or very narrow emission band, which reduces the need for filtration to separate the detection and stimulation spectral windows. These stimulation sources further have the advantages of being focusable to narrow spots and high power densities, which greatly reduces the readout time. However, laser sources are often relatively expensive, are sensitive to temperature, and can have long-term stability issues.

Feldspar measurements are generally obtained using infrared (800–900 nm) LED stimulation at ~ 200 milliwatts per square cm (mW/cm^2). For quartz measurements optical stimulation using LEDs is usually obtained using blue (470 nm) and green (520 nm) stimulations at power densities typically varying between 50 and $100 \text{ mW}/\text{cm}^2$. Jain (2009) suggested the use of a violet laser diode (405 eV) to extend the age range using quartz by probing deeper traps not accessible by blue light stimulation. In single-grain dating applications, solid state lasers emitting at 532 and 830 nm are used as stimulation light sources (Duller et al. 2003). The power densities at the sample for these light sources are estimated to be >2 orders of magnitude higher than those achievable with conventional LEDs.

Heating System

In TL dating it is important to be able to heat the samples reproducibly using adjustable (although usually constant) heating rates. The ability to vary the heating rates is particularly important for understanding TL processes. Although OSL is an optical method, samples usually require some thermal pretreatment to be able to compare the luminescence resulting from the natural and regenerated doses (e.g., Ankjærgaard et al. 2006). In quartz and feldspar OSL dating, for instance, it is customary to preheat the samples in the range of $160\text{--}320$ °C. Quartz OSL signals are also generally measured at an elevated but constant temperature (125 °C) to improve the signal-to-noise ratio. Most luminescence dating systems can heat up to 700 °C using heating rates ranging between 0.01 and 10 K/s. From a purely instrumental point of view, it is beneficial to perform heatings above 200 °C in a N_2 atmosphere to prevent oxidization of the heating element. In TL measurements to high temperatures, it has the further advantage of reducing spurious signals.

Irradiation Sources

In luminescence dating the measured natural luminescence signal is converted into an absorbed dose by comparison with regenerated signals induced in the laboratory by administering known doses to the sample. These signals can be regenerated using for instance gamma, beta, or alpha emitters. For practical reasons it is beneficial to be able to perform in situ irradiations. Due to radiation protection issues, beta emitters, particularly $^{90}\text{Sr}/^{90}\text{Y}$, are usually preferred as in situ

reference sources. The maximum $^{90}\text{Sr}/^{90}\text{Y}$ electron energy is 2.27 MeV and the mean electron energy is about 600 keV. Two of the major disadvantages of using a beta source are that the dose rate is fixed and that it may not provide a spatially uniform dose across the sample area (e.g., Spooner and Allsop 2000; although this disadvantage is not so important with a new type of $^{90}\text{Sr}/^{90}\text{Y}$ sources). In contrast, X-ray sources have electronically adjustable dose rates and have been shown to have a high degree of spatial uniformity and are easily shielded. However, X-ray sources are not widely used in luminescence dating, because the dose rate is highly sample dependent, probably because of high local ionization effects (Thomsen et al. 2006; Jain et al. 2007). It has been suggested that by hardening the X-ray spectrum, one can get rid of this sample dependency, but this suggestion has not yet been thoroughly tested. Alpha sources (primarily ^{241}Am) are only used in fine-grained (4–11 μm) polymineral dating and only if one wishes to determine the a-value (alpha to beta efficiency) for the samples in question.

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Amino Acid

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Definition

An organic compound containing an amino group (NH₂), a carboxylic acid group (COOH), and any of various side groups, having the basic formula NH₂CHRCOOH.

Amino acids are organic compounds composed of carbon, oxygen, hydrogen, and nitrogen in a specific structure where a central carbon atom is surrounded by a carboxyl group, an amino group, and a side chain that may be a single hydrogen or a more complex chain with multiple carbon-bearing entities. The structure common to all amino acids is shown in Fig. 1. Approximately 20 common amino acids are found in nature, and they combine in sequences of varying lengths to form peptides and proteins that have specific biochemical functions. Amino acids are found in a variety of geological samples and play a role in understanding chemical evolution, the formation and alteration of organic material in sediments, and geochronology (Goodfriend et al. 2000).

The role of amino acids in geochronology is based on the phenomenon of isomerism. Amino acids can exist in two isomeric forms, commonly referred to as “left handed” and “right handed.” These two forms are possible because the central carbon to which the four different side chains are bonded is asymmetric: two mirror-image configurations around this central carbon are possible, and these two are not geometrically equivalent.

Amino acids are found in sediments, soils, and in many common biominerals, as constituents of the structural proteins used by organisms such as mollusks, corals, foraminifera, etc., to synthesize the mineral phase. Amino acids are also found in bone, teeth, and wood. In most cases, the amino acids incorporated into the biomineral during growth are of the 100 % left-handed configuration. Upon death of the organism, these amino acids begin the process of racemization, or conversion from the 100 % left-handed form into an equilibrium mixture of 50 % of each of the two forms. The rate at which this reaction occurs is influenced by many factors, including temperature, sample type, alteration of the sample during its burial history, and specific rates of breakdown of the proteins that are preserved within the mineral matrix of the analyzed samples. Common amino acid racemization (AAR) studies include the use of foraminifera from deep-sea sediments (► [Amino Acid Racemization, Marine Sediments](#)), marine mollusks from coastal deposits (► [Biostratigraphy](#); ► [Amino Acid Racemization, Coastal Sediments](#)), and snails, eggshells, or ostracodes from terrestrial environments (► [Fluvial and Lacustrine](#); ► [Arctic](#); ► [Amino Acid Racemization, Egg Shell](#)). The timescale of these studies ranges from a few hundred years to over a million years, depending on the average temperatures to which samples have been exposed. These biominerals function to isolate the amino acids from the surrounding environment. Wood, soils, and bulk sediments also have been used in some AAR geochronological studies, with mixed success because of the open-system nature of these samples.

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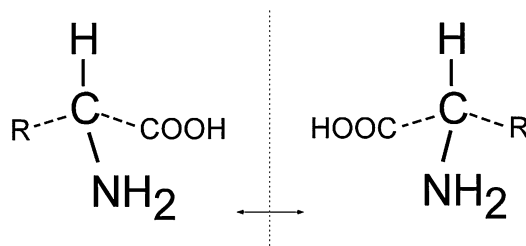


Fig. 1 Mirror-image relation between the two configurations of amino acid molecules. The four side chains are bonded to the central carbon atom at the corners of a tetrahedron. The two forms are geometrically distinct; hence the conversion of one form to the other requires breaking a bond and reassembling the amino acid as the other form. H = hydrogen; COOH = carboxyl group; NH₂ = amino group; R = one of many possible side chains that define the different amino acids

Radiocarbon (¹⁴C) dating (Cross-Reference) usually involves extracting carbon-bearing material (either organic carbon or carbonate carbon) from samples that are to be dated. In some cases, it is preferable to extract the amino acid component from these samples as a test of the integrity of the ¹⁴C result (Hatte et al. 2012). Comparison of ¹⁴C dates obtained on a bulk sample and the amino acid fraction of that same sample provide an indication of the integrity of the sample, as the amino acids (bound within the biomineral) would be expected to be less vulnerable to contamination from external sources (Marom et al. 2012).

Cross-References

- ▶ [Amino Acid Racemization, Arctic Environment](#)
- ▶ [Amino Acid Racemization, Biostratigraphy](#)
- ▶ [Amino Acid Racemization, Coastal Sediments](#)
- ▶ [Amino Acid Racemization Dating](#)
- ▶ [Amino Acid Racemization, Eolianites](#)
- ▶ [Amino Acid Racemization, Fluvial and Lacustrine Sediments \(AAR\)](#)
- ▶ [Amino Acid Racemization, Loess and Glacial Sediments \(AAR\)](#)
- ▶ [Amino Acid Racemization, Marine Sediments](#)
- ▶ [Amino Acid Racemization, Ostrich Egg Shell](#)
- ▶ [Amino Acid Racemization, Paleoclimate](#)
- ▶ [Radiocarbon Dating](#)

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Feldspars

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Feldspars are the most ubiquitous minerals in the Earth's crust. They are unique dating targets, in the fields of luminescence and **K-Ar/Ar-Ar** geochronology, as mineral grains in sediments and rocks. Both as grains of sediment and as grains in rocks.

Feldspars are compositionally symbolized as **MT₄O₈** where **M** are **K**, **Na**, and **Ca** and **T** are **Si** and **Al**. End-members composition for alkali feldspars are (**K**, **Al**) **Si₃O₈** (microcline, sanidine) and (**Na**, **Al**) **Si₃O₈** (albite). Plagioclases represent a continuous solid solution with end-members composition between albite and anorthite (**CaAl₂Si₂O₈**).

Feldspars are known as framework silicates, in which corner-sharing (**Al**, **Si**) **O₄** tetrahedra form crankshaft-like chains, assembled along their *a* axis. Cross-linking generates large coordination sites occupied by the charge-compensating cations (Fig. 1).

A most interesting aspect in feldspar mineralogy is in the distribution of **Al** and **Si** in tetrahedral sites. For the K-feldspars, complete disorder is observed for the high-temperature monoclinic sanidine, with an equal probability of finding **Al** at any T sites. At the other extreme, in ordered triclinic microcline, **Al** is found fitting preferentially in T₁ sites.

Due to the inherent complexity of natural crystals, the solid-state physics of feldspar luminescence is poorly known (Krbetschek et al. 1997; Baril 2002). Charge defects have been mostly detected along **Al-O¹⁻-Al** bridges, a likely candidate at the origin of the blue luminescence emission commonly selected in dating K-feldspar. Yellow-green (**Mn²⁺**) and red (**Fe³⁺**) emissions are clearly linked to specific recombination centers (Krbetschek et al. 1997; Baril 2002). Identification of electron traps has proven challenging. A good candidate at this stage is substitution of **Ti⁴⁺** for **Al³⁺** (T site) (Krbetschek et al. 1997; Baril 2002). The phenomenology of feldspar luminescence comprises a distinct instability of latent luminescence over geological time known as anomalous fading. Proposed culprits include **Al/Si** disorder, tunneling-prone electron traps, and instability of recombination centers (► [Feldspar Infrared Stimulated Luminescence](#)).

A minute fraction of the interstitial **K** undergoes radioactive decay to **⁴⁰Ar** and **⁴⁰Ca**. For thermochronometry applications, the argon diffusion processes are parameterized through laboratory step-heating experiments. Thermal diffusion of **Ar** in feldspar is controlled by M-O and O-O lattice configurations, vacancies, and linear and planar defects (Cassata and Renne 2013).

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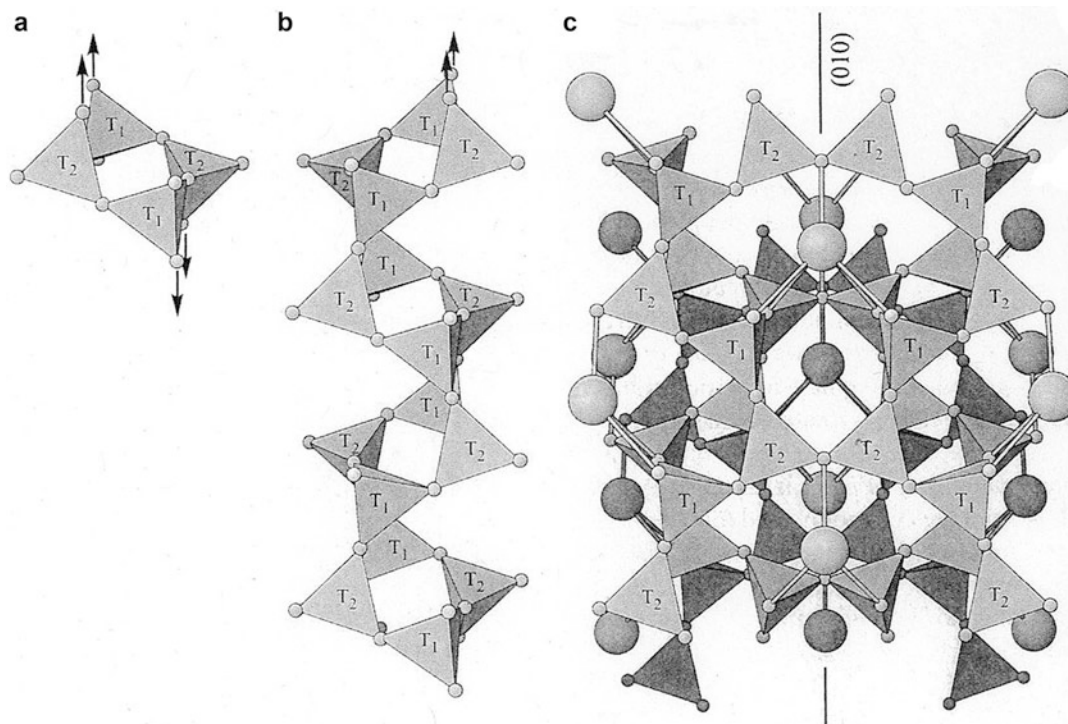


Fig. 1 Idealized feldspar structure, modified from Nesse (2012). M sites are locations of K, Na, or Ca; T sites are locations for either Al or Si; O sites are oxygen locations

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Potassium-Argon (Argon-Argon), Structural Fabrics

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Definition

$^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of structural fabrics: The application of $^{40}\text{Ar}/^{39}\text{Ar}$ methods to date development of structural fabrics in geologic samples.

Introduction

Structural fabrics develop during rock deformation at variable pressures (P), temperatures (T), fluid compositions (X), and time (t). Structural fabrics are represented in rocks by features such as foliations and shear zones developed at the mm to km scale. In ideal cases, the P-T-X history of a given structural fabric can be constrained using stable isotope, cation exchange, and/or mineral equilibria thermobarometry (Essene 1989). The timing of structural fabric development can be assessed qualitatively using geologic field observations or quantitatively using isotope-based geochronology. High-precision geochronology of the thermal and fluid flow histories associated with structural fabric development can answer fundamental geologic questions including (1) when hydrothermal fluids transported and deposited ore minerals, (2) fault activity and displacements, (3) the timing and duration of orogenic stages, and (4) the rates and frequency of these and other geologic processes.

Radioisotope systems (e.g., U–Pb, Rb–Sr, Sm–Nd) that quantitatively retain radiogenic isotopes in minerals that formed at relatively high temperatures ($>500\text{ }^{\circ}\text{C}$) are necessary for dating of structural fabrics that developed deep within the crust. For example, isotope geochronology of large-scale shear zones that define major crustal boundaries in the Grenville Province of Ontario, Canada, indicates that these well-developed structural fabrics define narrow time intervals of Neo- and Mesoproterozoic orogenic compression and extension (e.g., van Breemen and Hanmer 1986; van Breemen et al. 1986; Cosca et al. 1991, 1992; Mezger et al. 1991; van der Pluijm et al. 1994).

Isotopic dating of structural fabrics developed at shallower crustal levels requires isotope geochronometers that are sensitive to rock deformation at lower temperatures. The K–Ar geochronometer, including the $^{40}\text{Ar}/^{39}\text{Ar}$ method (McDougall and Harrison 1999), is well suited for isotopic dating of structural fabrics developed close to the brittle-ductile transition zone ($\sim 250\text{--}\sim 400\text{ }^{\circ}\text{C}$) because such rocks often contain potassium-bearing minerals including mixed-layer illite/smectite, biotite, and muscovite that quantitatively retain radiogenic argon ($^{40}\text{Ar}^*$) at or below $\sim 400\text{ }^{\circ}\text{C}$.

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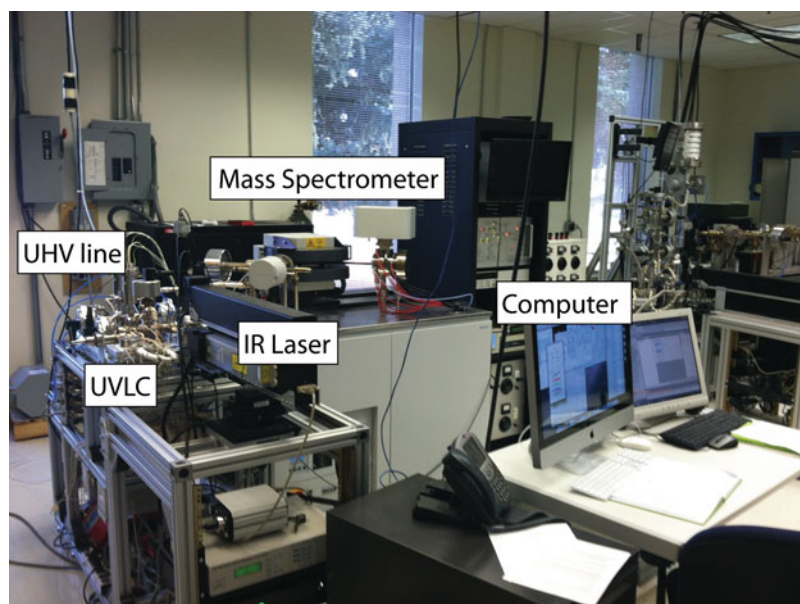


Fig. 1 Photograph of the USGS $^{40}\text{Ar}/^{39}\text{Ar}$ laboratory in Denver, CO. The $^{40}\text{Ar}/^{39}\text{Ar}$ system shown includes two lasers (IR and UV) for liberating Ar from rock and mineral samples. The UV laser has been removed for clarity (the position of the UV laser chamber (UVLC) is indicated). Setup and control of the $^{40}\text{Ar}/^{39}\text{Ar}$ experiments, including automation of the mass spectrometer, lasers, and UHV gas extraction line, is done using computers

$^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology of Structural (Deformation) Fabrics

$^{40}\text{Ar}/^{39}\text{Ar}$ Methods

Dating structural fabric using $^{40}\text{Ar}/^{39}\text{Ar}$ methods can be approached either by incrementally heating separated mineral grains with a furnace or infrared (IR) laser or by in situ laser ablation within small polished rock samples (thereby preserving textural context), with an IR or ultraviolet (UV) laser. The U.S. Geological Survey (USGS) system in Denver (Fig. 1) consists of both an IR laser (CO_2 , wavelength = 10.6 μm) and an UV laser (ArF exciplex, wavelength = 193 nm) attached to an ultrahigh vacuum (UHV) gas extraction system and mass spectrometer equipped with five Faraday detectors and a single compact discrete dynode ion multiplier. Samples for in situ analysis are prepared from polished rock chips, several mm on a side. One or more chips are irradiated by fast neutrons in a nuclear reactor and are placed in a laser sample chamber (Fig. 2) with a window that is transparent to 193 nm UV light. For in situ analysis, UV lasers are preferred over IR lasers because the shorter wavelengths results in minimal collateral heating of adjacent grains within the sample. Because small gas concentrations are liberated during UV laser ablation ($\sim 10^{-16}$ to $\sim 10^{-20}$ mol), isotopic measurements are performed by static mass spectrometry using a single ion multiplier.

Multigrain $^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology

Determining when foliations and shear bands develop is typically done by separating and analyzing pure, multigrain mica samples using either K–Ar or $^{40}\text{Ar}/^{39}\text{Ar}$ methods (e.g., Itaya and Takasugi 1988; Kelley 1988; Hames and Cheney 1997; Jaboyedoff and Cosca 1999; Mulch et al. 2004). Several multigrain $^{40}\text{Ar}/^{39}\text{Ar}$ studies of naturally deformed rocks have demonstrated that smaller grains yield younger ages (e.g., Kligfield et al. 1986; Kelley 1988; Goodwin and Renne 1991; Hess et al. 1993; Kirschner et al. 1996; Mulch et al. 2002; Markley et al. 2002). These multigrain studies

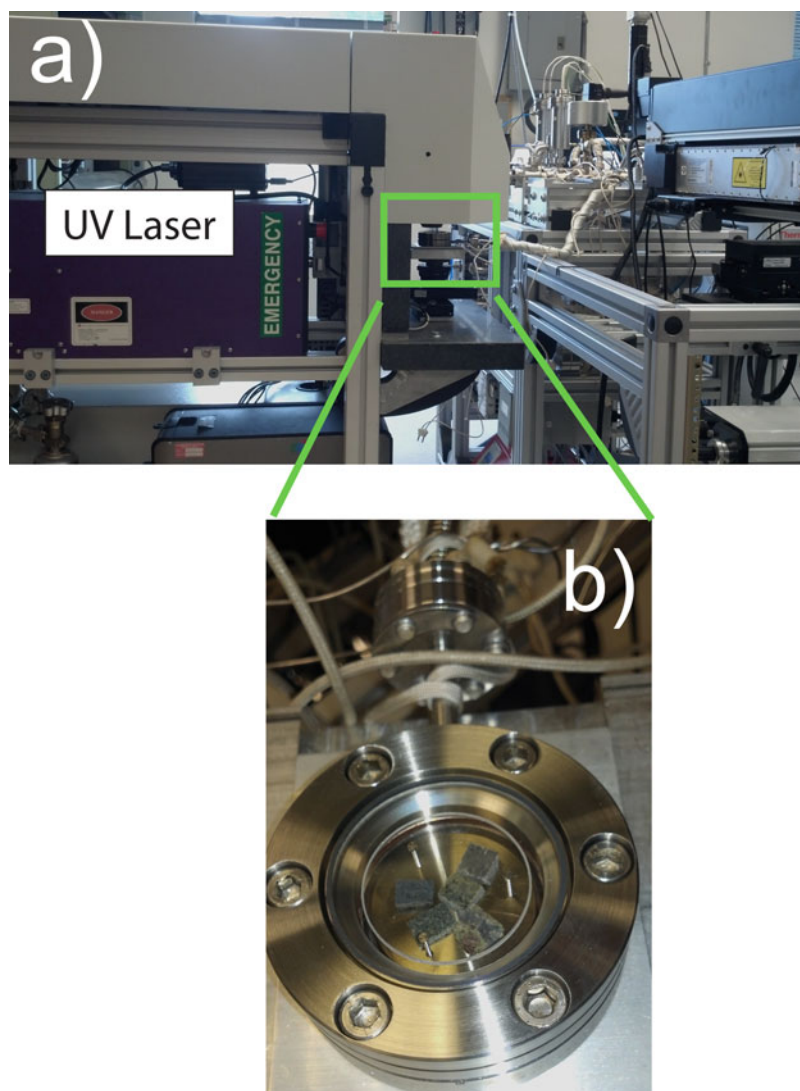


Fig. 2 Photograph of (a) UV laser attached to the extraction line and (b) expanded view from the top of the UVLC containing samples for analysis

show that the mean radius of physically separated grains reasonably approximates the effective length scale of $^{40}\text{Ar}^*$ diffusion, such that different-sized grains from the same sample reflect progressive cooling of the rock and closure to $^{40}\text{Ar}^*$ diffusion. Submicroscopic defects form in minerals during rock deformation (Gapais and White 1982; Passchier and Trouw 2005) and exert a nontrivial effect on intragrain $^{40}\text{Ar}^*$ retention and $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Lee 1995; Kramar et al. 2003). In situ UV laser ablation $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of individually deformed mineral grains offers a direct means of assessing the timing of deformation, the effective length scales for $^{40}\text{Ar}^*$ diffusion, and thermal histories (Cosca et al. 2011).

In Situ $^{40}\text{Ar}/^{39}\text{Ar}$ Geochronology

In situ $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology has been applied to investigate structural fabrics such as pseudotachylytes that formed rapidly under brittle conditions (e.g., Sherlock and Hetzel 2001) as well as ductilely deformed, slowly cooled rock (e.g., Hodges et al. 1994). The following examples, one

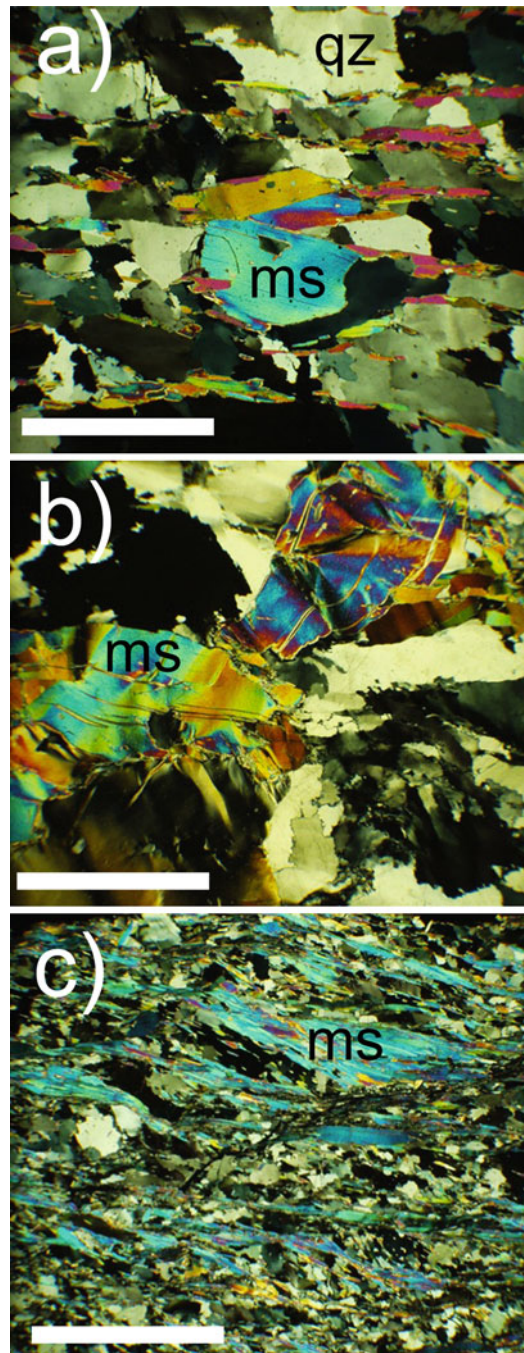


Fig. 3 Photomicrographs of white mica contained in typical structural fabrics. (a) Large, white mica porphyroclast that rotated into a planar shear zone defined by the smaller micas. (b) Strongly deformed white mica porphyroclasts with nonuniform optical properties suggest the presence of submicroscopic defects. (c) White mica porphyroclasts (fish) displaying evidence of internal size reduction as they were rotated into a shear zone fabric. *ms* muscovite, *qz* quartz. All scale bars are 1 mm

with mineral overgrowths and two involving internal mineral deformation, illustrate how intragrain $^{40}\text{Ar}/^{39}\text{Ar}$ age variations from different structural fabrics can be used to interpret geologic histories.

Overgrowths and Fluid Flow

Isotopic dating of texturally and compositionally distinct mineral overgrowths or strain fringes provides a direct measure of rock deformation, fluid flow, and mineral growth (e.g., Muller et al. 2000; Sherlock et al. 2005; Wells et al. 2008). For example, the Proterozoic Telemark detachment in southern Norway contains white mica porphyroclasts (mica fish) that formed during an initial period of upper amphibolite-grade deformation, and during subsequent greenschist facies deformation these grains developed compositionally distinct overgrowths (Mulch et al. 2005). In situ UV laser ablation $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of the white mica overgrowths revealed that they developed over a period of approximately 10 my, and that occurred roughly 10 my after closure to argon diffusion in the mineral cores. Together with oxygen isotope values in deformed quartz, these observations indicate that a compositionally distinct fluid was present during deformation that facilitated growth or recrystallization of the mica overgrowths.

White Mica Porphyroclasts in Shear Bands

In situ UV laser ablation $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of mica porphyroclasts in shear bands provides a means of dating past movement (e.g., Mulch and Cosca 2004) and potentially provides a means of reconstructing paleoelevations (Mulch et al. 2004). Greenschist facies micaceous quartz mylonites often contain large (mm-sized) porphyroclasts of variably deformed white mica (Fig. 3a, b). These rocks often develop C'-type shear bands (Berthé et al. 1979) that cut across earlier formed foliations and surviving porphyroclasts. In some shear bands, the so-called mica fish porphyroclasts develop and may undergo progressive mechanical grain size reduction during shearing, resulting in smaller segments of mica (Fig. 3c). This process of grain size reduction has been dated in the Pogallo shear zone of northern Italy (Mulch et al. 2002) in which mica porphyroclasts yielded in situ UV laser ablation $^{40}\text{Ar}/^{39}\text{Ar}$ dates that became younger as both the physical grain size and the length scale for $^{40}\text{Ar}^*$ diffusion decreased.

The extent of structural fabric development and defects on $^{40}\text{Ar}^*$ retention in micas within shear bands at the sub-grain scale can be assessed by in situ UV laser ablation of individual mica porphyroclasts. For example, over 150 individual UV laser ablation $^{40}\text{Ar}/^{39}\text{Ar}$ analyses within one large mica porphyroclast from a Carboniferous quartz-mica pegmatite layer reveal $^{40}\text{Ar}/^{39}\text{Ar}$ dates that correlate, and become younger, with position relative to incipient shear bands within the mica fish (Kramar et al. 2001). When examined by transmission electron microscopy, this mica fish contains abundant stacking faults or microstructural distortions caused by partial dislocations and localized charge imbalances (Kramar et al. 2003). The interconnectivity of these line defects decreases retentivity of $^{40}\text{Ar}^*$ by several orders of magnitude and can explain the range of intragrain $^{40}\text{Ar}/^{39}\text{Ar}$ dates intermediate between known periods of Carboniferous and Oligocene-Miocene deformation (Kramar et al. 2001, 2003).

Summary

$^{40}\text{Ar}/^{39}\text{Ar}$ studies of structural fabrics have shown that retention of $^{40}\text{Ar}^*$ in naturally deformed rock is sensitive to the intensity, duration, temperature, and presence of fluids during rock deformation. Understanding the link between $^{40}\text{Ar}/^{39}\text{Ar}$ ages and microstructures in deformed rock remains a fertile ground for continued research.

Cross-References

- Potassium-Argon (Argon-Argon), Alpine terranes
- Potassium-Argon (Argon-Argon), Clays and Glauconites
- Potassium-Argon (Argon-Argon), Metamorphic Terranes
- Potassium-Argon (Argon-Argon), Minerals
- Potassium-Argon and Argon-Argon Dating

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Luminescence Dating

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Definition

Luminescence – emission of light from a semiconductor or insulator in response to some form of stimulation such as heat or light. In the context of using luminescence for dating, the luminescence signal arises from the release of energy stored from prior exposure to ionizing radiation such as alpha, beta, or gamma radiation. Thus, luminescence provides a mechanism for measuring the amount of ionizing radiation a sample has been exposed to.

Thermoluminescence (TL)	Emission of luminescence in response to heating of the sample.
Optically Stimulated Luminescence (OSL)	Emission of luminescence in response to exposing the sample to light. In the laboratory this light is normally restricted to a narrow range of wavelengths.

Introduction

Radioactivity is ubiquitous in the natural environment. Luminescence dating exploits the presence of radioactive isotopes of elements such as uranium (U), thorium (Th), and potassium (K). Naturally occurring minerals such as quartz and feldspars act as dosimeters, recording the amount of radiation to which they have been exposed.

A common property of some naturally occurring minerals is that when they are exposed to emissions resulting from radioactive decay (e.g., alpha, beta, and gamma radiations), they are able to store within their crystal structure a small proportion of the energy delivered by the radiation. This stored energy increases as exposure to radioactive decay continues through time. At some later date this energy may be released, and in some minerals this energy is released in the form of light. This light is termed luminescence.

What makes this a useful phenomenon for dating, and what event is being dated? The answer lies in the fact that this energy stored in minerals can be reset by two processes. The first is by heating the sample to high temperatures (typically above 300 °C, as would occur during firing of pottery, or in a hearth). The second process is exposure of the minerals to daylight, as may occur during erosion, transport, and deposition of sediments. Either of these processes will release preexisting energy stored within a mineral and therefore set the “clock” to zero. Thus, in luminescence dating, the event being dated is this resetting, either by heat or by exposure to light.

Major applications utilizing the resetting of the signal by heat include dating when a piece of pottery was produced or when stones in a hearth were last heated. The application to burnt stones includes both stones that were used to form a hearth, but also a large number of important studies have dated flint tools that have inadvertently been burnt. Luminescence dating is now most commonly used to date the last exposure to sunlight of sediments; this is assumed to correspond

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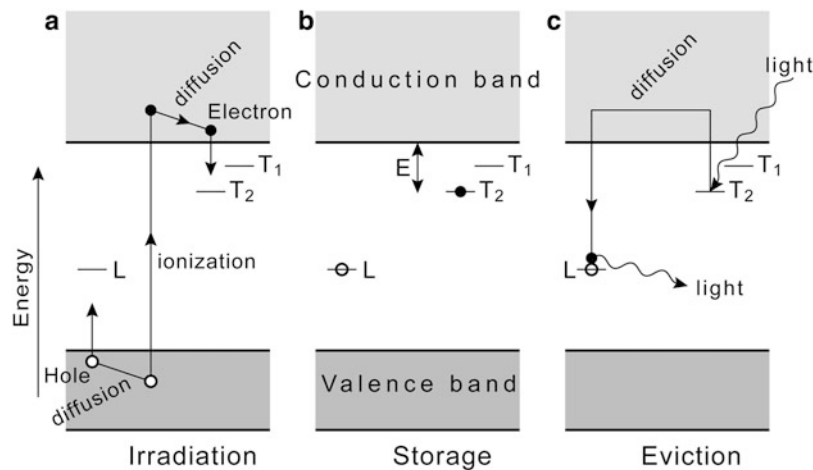


Fig. 1 Schematic bandgap diagram of the processes involved in ionization, storage, and eviction of charge that underpin the production of luminescence signals in crystalline materials (Adapted from Aitken 1985). Further details about the sequence of processes illustrated here are given in the text

with the time of deposition of the sediment. The method is ideally suited to aeolian sediments where there is ample opportunity for sediments to be exposed to daylight such as coastal and desert dunes (see “► [Luminescence, Coastal Sediments](#)” and “► [Luminescence, Desert Dunes](#)”) and windblown dust either deposited on land to form loess (see “► [Luminescence, Loess](#)”) or in the oceans (see “► [Luminescence, Deep Sea Marine and Lacustrine](#)”). Provided that due care is taken with measurements (as detailed below), the method can also be applied to fluvial sediments (see “► [Luminescence, Fluvial Sediment](#)”), and in recent years the method has been extended to look at glacially derived materials (see “► [Luminescence, Glacial Sediment](#)”), though great care is needed in such applications to assess whether the sedimentary grains were exposed to sufficient daylight at deposition to reset the luminescence signal.

Measurements of the brightness of the luminescence signal can be used to calculate the total amount of radiation that the sample was exposed to during the period of burial. If this is divided by the amount of radiation that the sample receives from its surroundings each year, then this will give the duration of time that the sample has been receiving energy:

$$\text{Age} = \frac{\text{Total energy accumulated during burial}}{\text{Energy delivered each year from radioactive decay}} \quad (1)$$

The S.I. (Système International) unit of absorbed radiation is the Gray, abbreviated to Gy. It is a measure of the amount of energy absorbed by a sample, or its dose, and has the units Joules per kilogram. Luminescence measurements are used to calculate the total absorbed dose as measured in the laboratory. The name given to the quantity is the equivalent dose (D_E). The amount of energy absorbed per year from radiation in the environment surrounding the measured material (known as the dose rate) can either be derived by directly measuring the amount of radioactivity or by chemically analyzing the surrounding material and calculating the concentration of radioisotopes in it; this has the units of Gray per year. Thus, the age equation for luminescence can formally be expressed as

$$\text{Age (years)} = \frac{\text{Equivalent dose (Gy)}}{\text{Dose rate (Gy per year)}} \quad (2)$$

A range of different minerals emit luminescence, but the majority of dating applications have used quartz, feldspars, or mixed phases of SiO_2 in flint. A number of different luminescence signals can be obtained from each of these minerals (or rocks in the case of flint). The result is an increasingly diverse range of luminescence dating methods that are possible. They all share the same basic principles outlined above, but the age range over which they can be applied, and the details of their application vary. To understand the reason for these differences and some of the details of the method, it is necessary to understand more about the physical basis of the luminescence signals that are observed.

Physical Basis

Luminescence occurs as result of energy stored within a crystalline solid being released and being emitted in the form of a photon of light. To understand this process, Fig. 1 shows a schematic representation of the band structure of an insulator or semiconductor and various processes that occur within and among the bands. In such materials the valence band is fully occupied by electrons, while no electrons reside in the conduction band. Further information about the band structure of crystalline insulators and semiconductors is given in see “► [Band Structure](#).” There is a forbidden energy gap between the valence and the conduction band and most electrons are unable to reside in this gap. However, if chemical impurities exist within the crystal or other structural defects are present, then these may give rise to traps within the forbidden gap (marked T_1 and T_2 on Fig. 1a) where electrons can be stored in an excited state.

Ionizing radiation interacting with this theoretical crystal can transfer energy to an electron in the valence band, and this process of ionization will excite the electron into the conduction band (Fig. 1a) and leave a hole in the valence band. The electron is unable to remain in the conduction band and one of two events will follow. Either the electron will immediately de-excite to the valence band, releasing the energy absorbed from the radiation, or the electron in rare cases may lose a small amount of energy and become trapped at T_1 or T_2 within the forbidden gap as shown in Fig. 1a. Similarly, the hole created in the valence band by the eviction of an electron can diffuse through the crystal and may become trapped at another class of defects, called recombination centers. A proportion of these recombination centers are capable of producing luminescence (“L” on Fig. 1a). The net effect is that a proportion of the energy deposited by the radioactivity has become stored within the crystal structure. As further ionization occurs, the number of electrons stored in traps (e.g., T_1 or T_2), and hence the amount of energy stored, will increase. If the trap is stable, then these electrons may be stored for periods of thousands to millions of years (Fig. 1b). The stability of the charge in the trap depends upon the amount of energy required to excite charge out of the trap. This energy (indicated by “E” in Fig. 1b) varies from one trap to another. Generally, the deeper the trap, the more stable it is.

The electrons stored in the defects within the forbidden gap can be released by providing sufficient energy (such as light or heat) to excite them into the conduction band. From there they must relax and may recombine with a hole stored at a luminescence center “L” (Fig. 1c). This recombination may result in the emission of light – this is the luminescence signal that is observed.

Thermoluminescence (TL)

Historically (see “► [Luminescence Dating, History](#)”), the first method used to measure luminescence was by heating the sample at a fixed rate (typically between $1\text{ }^\circ\text{C/s}$ and $5\text{ }^\circ\text{C/s}$) from room temperature up to temperatures varying between $450\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$, depending upon the mineral.

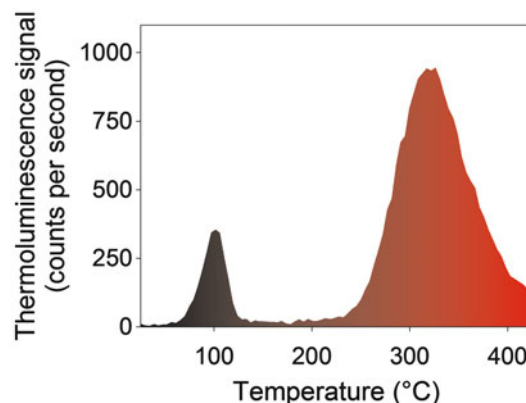


Fig. 2 A typical thermoluminescence (TL) measurement, known as a glow curve. The intensity of the TL signal is shown as a function of the sample temperature as it is steadily increased from room temperature to 450 °C at a rate of 5 °C/s

The emission is termed thermoluminescence (TL) and a graph showing the luminescence signal emitted as a function of temperature (commonly referred to as a glow curve) consists of a series of peaks (e.g., Fig. 2). Each peak may be due to a single type of trap within the mineral being measured, but more commonly the signal is a composite of several traps. Although it is not always possible uniquely to identify the source of the electrons, it is normally true that the TL signal observed at higher measurement temperatures originates from traps that are deeper below the conduction band: this follows because more energy is required to release electrons from deeper traps than electrons released from traps at lower temperatures, and so this only occurs at higher measurement temperatures. A corollary of this is that electrons in deeper traps are more stable than those in shallower traps. For instance, Fig. 2 shows a TL measurement of quartz. The electrons in the trap giving rise to the TL peak observed at ~110 °C are relatively unstable and at room temperature have a mean lifetime of ~20 h, making them useless for dating. In contrast, measurements suggest that the electrons giving rise to the TL peak observed at ~325 °C are stable over many millions of years. These two peaks could be thought of as being derived from traps T_1 and T_2 , respectively, in Fig. 1. The stability of the deeper trap has been confirmed by dating of sediments up to almost a million years old, and it is this trap that is the focus of most methods used for dating with quartz.

Optically Stimulated Luminescence (OSL)

A second way of stimulating the emission of luminescence is by exposing a sample to light. In ground breaking work, Huntley et al. (1985) shone the beam from an argon-ion laser emitting at 514 nm onto their samples of quartz and feldspar. They then observed the luminescence emitted at a wavelength of ~400 nm. This optically stimulated luminescence (OSL) signal occurs as soon as the sample is illuminated, and the intensity of the OSL signal decreases as electrons are removed from the traps as measurement continues (Fig. 3). Unlike TL, the OSL data typically obtained gives little indication from which traps the electrons have been released. Thus, prior to making an OSL measurement, it is important to thermally pretreat the sample so that a signal is obtained from the group of traps of interest. This is achieved by heating the sample prior to measurement so that the shallow traps, whose electrons are unstable over the burial period (e.g., T_1 in Fig. 1), are emptied, leaving only the electrons in deeper, stable traps (e.g., T_2 in Fig. 1). This thermal treatment is called a preheat.

The light used to stimulate the minerals is restricted to a narrow range of wavelengths, and this light must be prevented from reaching the sensitive light detector (the photomultiplier tube) used to

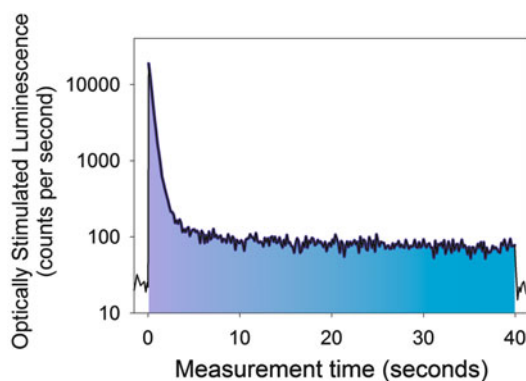


Fig. 3 A typical quartz optically stimulated luminescence (OSL) decay curve. When the optical stimulation source is first switched on, the OSL signal is large (~18,000 counts per second in this example) but then rapidly decreases as the charge stored in the traps is removed. Note that the vertical axis is on a log scale

measure the luminescence signal (see “► [Luminescence Dating, Instrumentation](#)”). This is because the light given off by the sample, the luminescence that is being measured, is emitted at a different wavelength from the stimulation light. Blue light-emitting diodes (LEDs) are commonly used for stimulation and will generate an OSL signal from both quartz and feldspar. An alternative method of stimulation is to use LEDs that emit beyond the visible part of the spectrum, in the infrared. These are the type of LEDs used for remote controls in televisions, and for luminescence work, those centered at 880 nm have been used extensively in infrared-stimulated luminescence (IRSL) dating of feldspar. OSL signals are produced but are more commonly referred to as infrared-stimulated luminescence (IRSL). IRSL is only observed from feldspars; quartz grains do not give an IRSL signal when the sample is measured at room temperature unless the quartz grains contain feldspar inclusions. The fact that pure quartz does not emit an IRSL signal at room temperature can be exploited to provide a method for assessing the purity of quartz separated for luminescence measurements.

In naturally occurring minerals, a range of different traps occur. In quartz it is thought that aluminum substituting for silicon within the SiO_2 structure is an important source of defects, though many other impurities are also important (e.g., Ge) (see “► [Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence](#)”). The relative concentration of these different types of trap varies from one sample of quartz to another. The result is that the intensity and detailed nature of the luminescence signal from quartz varies for different areas. Similarly, different minerals have different impurities (e.g., manganese in calcite) and thus different luminescence behavior. In feldspars the mechanisms by which luminescence is generated are thought to be more complex than in quartz, with some recombination from traps to luminescence centers not involving the conduction band (see “► [Feldspar Infrared Stimulated Luminescence](#)”).

The physical characteristics of the different traps control whether they are suitable for luminescence dating. Only some of the traps that are known in naturally occurring minerals are sensitive to light, while charge in others can only be evicted by heating the sample. Those traps which are sensitive to light are the ones that are most appropriate for dating sediments. Equally important is whether the charge stored within the traps is stable over the period of time that is being dated. A key consideration here is the depth of the trap below the conduction band. This can be measured as the energy required to excite an electron from the trap to the conduction band (marked as E on Fig. 1b). In general terms the deeper the trap (the greater the value of E), the more stable the trap.

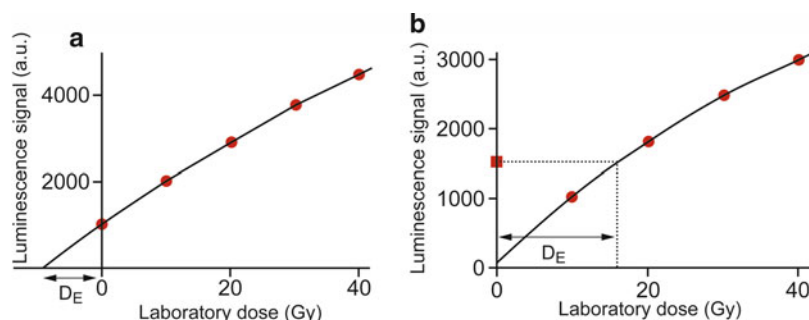


Fig. 4 (a) The additive dose method for determining equivalent dose (D_e). Red data points show luminescence measurements made after different laboratory irradiations. (b) The regenerative dose method for determining equivalent dose. The luminescence signal resulting from irradiation in nature (plotted as a square on the y-axis) is interpolated onto a dose response curve that is generated by making measurements after different laboratory irradiations

Measuring Equivalent Dose

In order to calculate the radiation dose that a sample has been exposed to (the equivalent dose, D_e), it is necessary to calibrate the signal using an artificial radiation source in the laboratory whose dose rate is known. The intensity of the luminescence signal arising from the dose received in nature can then be compared with the intensity of a luminescence signal following exposure to known radiation doses in the laboratory. There are two broad strategies for such measurements, additive dose methods and regeneration methods (Fig. 4).

In the additive dose method (Fig. 4a), the intensity of the luminescence signal arising from the dose absorbed in nature is measured. Additional measurements of the luminescence signal are then made after adding known radiation doses in the laboratory. The change in luminescence intensity with laboratory radiation is then fitted and extrapolated to the intersection with the x-axis to calculate what dose must have been absorbed by the sample prior to measurement of the natural – the D_e .

In the regeneration method (Fig. 4b), after measurement of the luminescence signal arising from exposure to radiation in nature, the sample has its luminescence signal reset (normally by exposure to an artificial light source), and then different laboratory radiation doses are given and the subsequent luminescence signal measured. The growth of the luminescence signal with laboratory dose is fitted, and the intensity of the signal resulting from exposure in nature is interpolated onto that curve in order to calculate D_e .

The value of D_e calculated by extrapolation in the additive dose method (Fig. 4a) can be very sensitive to the choice of which mathematical model is used to fit the dose response curve. Mathematically, the regeneration method is simpler since the natural signal (shown as a square on Fig. 4b) is being interpolated between measured data points, and not extrapolated.

Two broad approaches have been developed for making the luminescence measurements necessary for the additive dose or regenerative dose methods. When luminescence was first developed, a number of different subsamples, or aliquots, of each material would be prepared. Different laboratory doses would be given to each group of aliquots. Thus, multiple aliquots were required to calculate a single equivalent dose (D_e). Both multiple aliquot additive dose (MAAD) and multiple aliquot regenerative dose (MAR) methods have been used in the past. Duller (1991) was the first to propose practical methods where all of the measurements necessary to determine D_e could be made using a single aliquot. Since this innovation a series of important breakthroughs have been made, developing a variety of single-aliquot methods for feldspars (Duller 1995) and for quartz (Murray et al. 1997), and there has been a tendency for the majority of measurements to be made using single-aliquot methods.

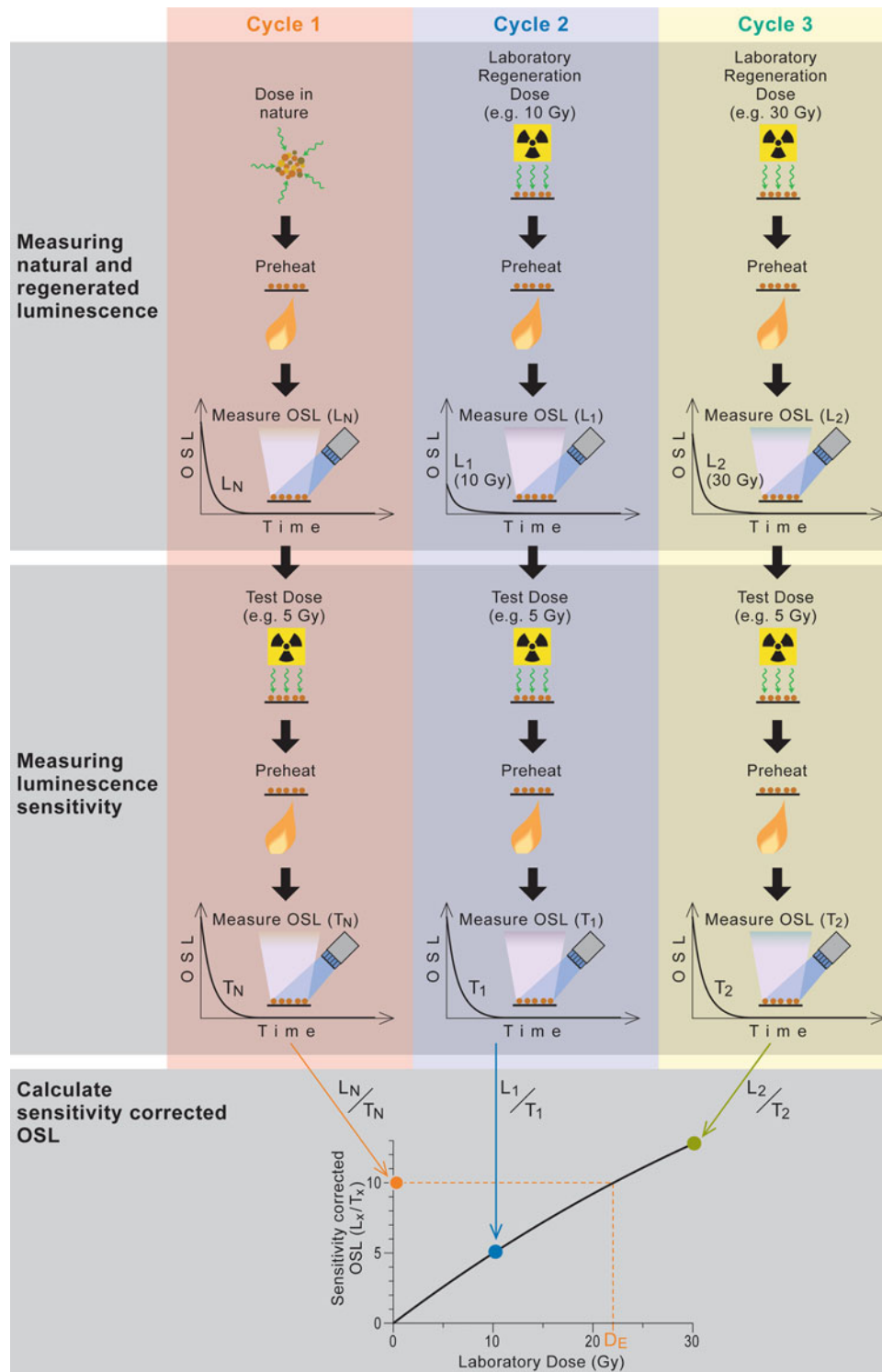


Fig. 5 Schematic of the single-aliquot regenerative dose (SAR) measurement protocol and how the different luminescence measurements are combined in order to determine the equivalent dose (D_e). The method was first developed by Murray and Wintle (2000) (Figure adapted from Duller (2008b))

A challenge when using single-aliquot methods is that the luminescence sensitivity, defined as the amount of light emitted per unit of absorbed radiation, may vary when repeated measurements are

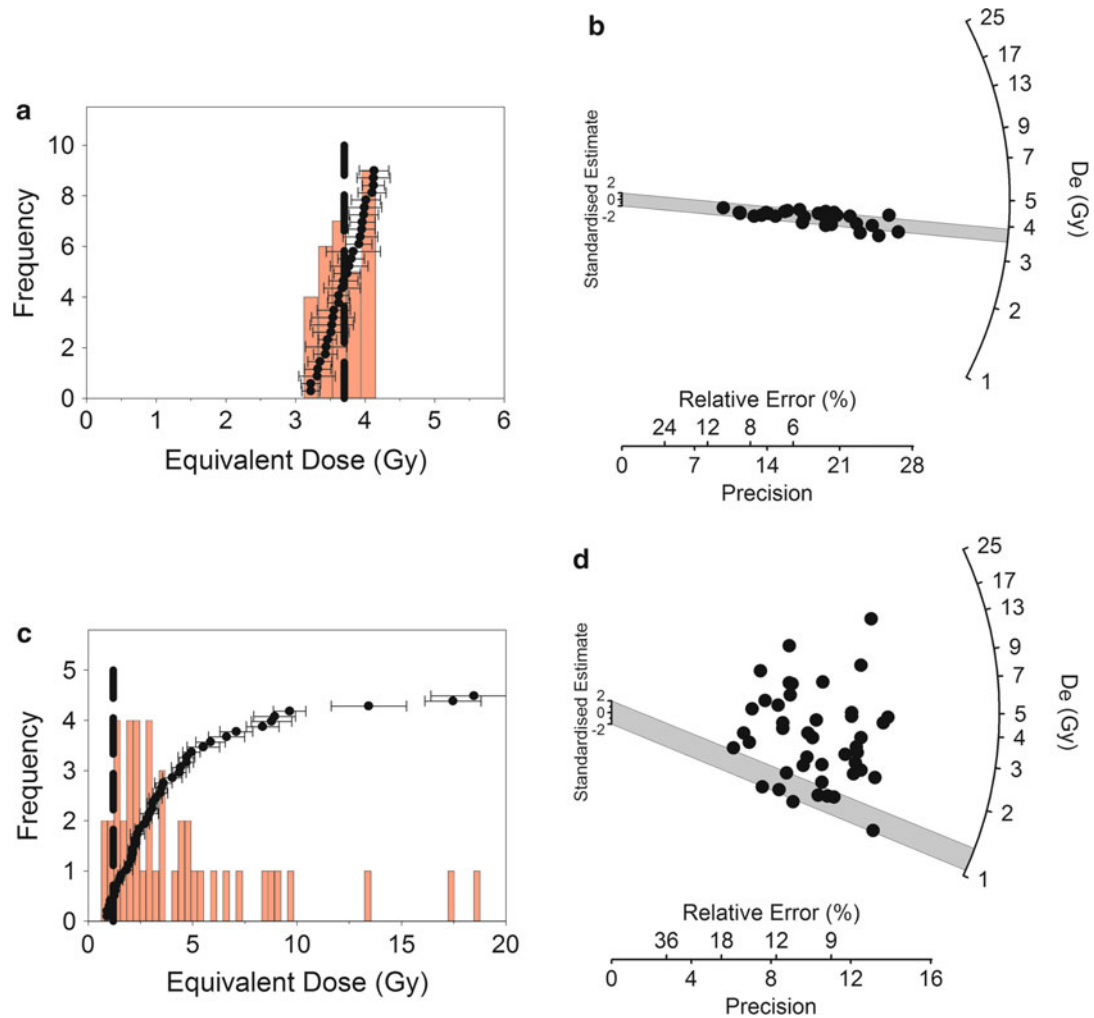


Fig. 6 Replicate measurements of equivalent dose (D_e) for two different samples. In each case the same data set is shown both as a histogram and as a radial plot. **(a, b)** Replicate measurements of D_e for an aeolian sample form a single population, and an average value can be used for calculating an age (shown by the vertical dashed line in **(a)** and the grey bar in **(b)**). **(c, d)** Fluvial samples (or other incompletely bleached samples) may exhibit much greater variability in D_e . High values (in this case above about 3 Gy) occur because some grains were not reset at deposition and thus inherited a signal. The value of D_e appropriate for calculating an age from this distribution can be found using statistical models and is shown in **(c)** as a vertical dashed line and by a grey bar in **(d)**

made. This problem became apparent when applying single-aliquot methods to quartz (e.g., Stokes et al. 2000). Early attempts to correct for this change in sensitivity used the response of the 110°TL peak in quartz (Murray and Roberts, 1998), but it became apparent that this signal did not completely mimic the changes in sensitivity of the OSL signal. The single-aliquot regenerative dose (SAR) method proposed by Murray and Wintle (2000) for quartz explicitly measures any change in luminescence sensitivity during repeated measurements by monitoring the OSL response to a test dose and corrects for these changes. Figure 5 summarizes the sequence of measurements that are undertaken. After measurement of the luminescence signal arising from irradiation in nature (L_n) or measurement of the luminescence signal arising from a laboratory dose (L_x) (shown at the top of the panel), the aliquot is exposed to a fixed radiation dose to test the luminescence sensitivity. This test dose is kept constant for any given aliquot, and the subsequent luminescence measurement (T_x) would be constant if there were no change in sensitivity. If sensitivity change does occur, then it can

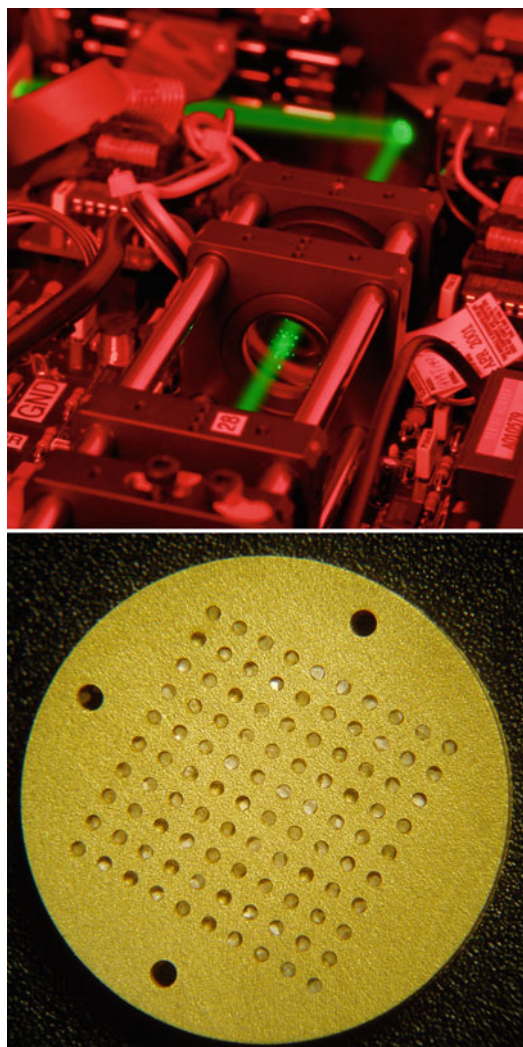


Fig. 7 *Upper*: Focused laser used to stimulate single grains. *Lower*: Sample holder (10 mm diameter) with a grid of 100 holes (each hole 300 μm in diameter). The focused laser strikes each hole in turn, measuring the OSL from each grain of quartz (Photos: G.A.T. Duller)

be seen as changes in T_x . A simple way to correct for these changes in sensitivity is to plot a dose response curve of the ratio of L_x divided by T_x as a function of laboratory radiation dose (bottom of Fig. 5). The critical development in Murray and Wintle (2000) was developing a protocol which made it possible to make all of these measurements using OSL signals.

Advantages of Single-Aliquot Measurements

The use of single-aliquot measurements makes it feasible to make replicate measurements of the D_e of a sample. It is common practice for 20–50 aliquots to be measured for a single sample. This makes it possible to determine whether the values of D_e for a sample are consistent with one another, or whether they show variability. For samples which were either heated uniformly or which were exposed to sufficient daylight at deposition to completely remove their signal, replicate D_e values will form a single population (Fig. 6a, b), and some measure of central tendency (e.g., the mean or weighted mean) can be calculated as used in the age equation (Eq. 2). More complex patterns are seen in samples where the amount of exposure to daylight at deposition varied from one grain to

another or where mixing of the deposit, for example, by bioturbation, has occurred. This is common for samples where the exposure to daylight is limited, as may be the case for fluvial or glacial samples (Fig. 6c, d). In this situation, where a measurement includes grains that were not bleached at deposition, the value of D_e obtained will be the sum of the dose acquired since deposition, plus an inherited signal whose size may vary from a few Gy to many tens of Gy. The result is a skewed distribution where the D_e value corresponding to deposition of the sediment is the lowest value observed. A range of statistical approaches have been proposed to deal with such situations (Galbraith and Roberts 2012). The most commonly used statistical model is the Minimum Age Model (MAM). Complex patterns may also be seen in replicate measurements of D_e if bioturbation has occurred and mixed sediments of different ages (Rink et al. 2013), in which case standard models to deal with this situation have not yet been developed.

An additional advantage of single-aliquot methods of equivalent dose determination is that the number of grains in each aliquot can be varied (Duller 2008a). Where samples consist of a complex mixture of grains with different D_e values, then it may be advantageous to make measurements on single mineral grains (see “► [Luminescence Dating, Single Grain Dose Distribution](#)”). This is not possible for silt-sized samples ($<90\text{ }\mu\text{m}$), but for sand-sized materials, it is possible either to handpick the grains or to use focused laser systems designed to make luminescence measurements on single grains (Fig. 7). Such single grain measurements have proved essential for dating some complex archaeological sites (Jacobs et al. 2008), glacial sediments (Duller 2006), and applications looking at rates of bioturbation in soils (Heimsath et al. 2002). Single grain measurements of quartz consistently show that only a small proportion of grains emit luminescence of sufficient intensity to be useful. It is common for 90 % of the luminescence signal that is emitted to originate in 5 % of the grains. In extreme cases less than 1 % of the grains may emit a signal of sufficient intensity to be useable. When making measurements of feldspars, a higher proportion of grains emit a luminescence signal, but this approach is still in its infancy.

Measuring Dose Rate

The denominator in the luminescence age equation Eq. (2) is the dose rate; this is a measure of the ionizing radiation energy that a sample has been exposed to each year during burial. This energy derives from two main sources (see “► [Luminescence Dating, Dose Rate](#)” and “► [Radiation Dose Rate](#)”). The first of these are naturally occurring radioisotopes which are found in the sediments making up the samples collected for dating. Alpha, beta, and gamma radiations are produced by a variety of radioisotopes, primarily associated with potassium, uranium, and thorium, and to a lesser degree rubidium. The second source of radiation is cosmic rays. These are high-energy particles that originate from high-energy sources in the universe such as supernovae and which bombard the earth and interact with atmospheric gas molecules to produce earth-surface showers of cosmic rays. Cosmic rays are critical in the formation of radiocarbon (see “► [Radiocarbon Dating](#)”) and form the basis for cosmogenic nuclide dating (see “► [Terrestrial Cosmogenic Nuclide Dating](#)”). In luminescence dating cosmic rays are significant because they are sufficiently energetic to excite charge into the conduction band and thus are part of the total radiation dose rate for a given sample.

Cosmic rays are absorbed as they pass through sediments, and thus, the dose rate due to cosmic rays is greatest near the surface and decreases in a predictable manner as samples are buried. Cosmic rays are weakly absorbed by the atmosphere, so cosmic dose rates are greater for samples at high altitude than those near sea level. There is also a weak latitudinal dependence because of interactions between cosmic rays and the Earth’s magnetic field. The cosmic dose rate can be easily calculated based on measurements of burial depth, altitude, longitude, and latitude, using equations described

by Prescott and Hutton (1994). Typical dose rates due to cosmic rays are 0.2–0.05 Gy/ka depending upon the depth of burial.

In most applications of luminescence dating, the greatest contribution to the total dose rate arises from the decay of radioisotopes in the immediate vicinity of the sample. The main elements of relevance here are potassium, uranium, and thorium. The radioactive isotope of potassium (^{40}K) undergoes a single decay to either ^{40}Ca or ^{40}Ar , emitting beta particles and gamma rays. Uranium (^{238}U and ^{235}U) and thorium (^{232}Th) have more complex decay patterns. Each of these three radionuclides is the parent isotope of a series of radioactive daughter isotopes (see “► [Radiation and Radioactivity](#)”) and they form three decay series. The different radioisotopes making up these decay series emit a combination of alpha, beta, and gamma radiations. These three types of radiation have very different properties. Alpha particles consist of two neutrons and two protons and are only able to penetrate very short distances ($\sim 10\text{--}40\text{ }\mu\text{m}$) in Earth materials. Beta particles are electrons, and these are able to penetrate up to 2 mm. Gamma rays are part of the electromagnetic spectrum and are able to penetrate up to 30 cm in rocks and sediments.

When calculating the dose rate, it is necessary to differentiate between the dose from radionuclides that are found inside the material being used for luminescence dating and the dose from radionuclides found in the sediment surrounding the material separated for dating. The former is known as the internal dose, and the latter the external dose. If luminescence measurements are made on grains of quartz separated from sediment, the internal dose is normally very small in comparison with the external dose, and in many cases it is assumed to be zero. In contrast if the luminescence signal from feldspars is used, these grains may contain up to 14 % by weight of potassium, and this yields a large internal dose which forms a critical part of the total dose rate to the grains.

An additional consideration in calculating the dose rate to a sample is the impact of the water content of a sample. In the case of sediments, there will be interstices between mineral grains, and depending upon the environmental conditions at a specific site, these interstices may either be wholly air-filled, wholly filled with water, or more commonly a mixture of the two. Water between grains absorbs a proportion of the radiation energy emitted by radionuclides and thus alters the dose rate. The impact of water upon alpha, beta, and gamma radiations is well understood and is an integral part of the process of calculating a dose rate. A useful rule of thumb is that a 1 % increase in the water content leads to approximately a 1 % increase in the luminescence age. It is therefore necessary to estimate the average water content of the sample during the period being dated. Estimating the water content of sediments during the entire period of burial can be a challenge, and uncertainty in this value is commonly one of the most important controls on the precision with which it is possible to calculate luminescence ages (see “► [Luminescence Dating, Uncertainties and Age Range](#)”).

There are two primary approaches for measuring the dose rate due to radionuclides: chemical methods and emission counting methods. A variety of chemical methods such as AAS, ICP-MS, and NAA are available. It is normal practice to measure only the concentration of K, U, and Th in samples and to assume that the U and Th decay series are in secular equilibrium (see “► [Radiation and Radioactivity](#)”). Emission counting methods directly measure alpha, beta, or gamma emissions from a sample. Alpha particles and gamma rays are emitted with specific energies which means that spectroscopic methods can be used to identify which radioisotope individual alphas and gammas originate from. Alpha spectroscopy is not commonly used because of the lengthy sample preparation procedure, but high-resolution gamma spectroscopy using high-purity germanium detectors is widely used. Beta particles arising from a specific isotope are emitted at a range of energies and thus spectroscopic methods are not possible. However, it is possible to measure the total beta dose rate and to account for the range of expected ranges of beta emission energy which occur with known



Fig. 8 Using a portable gamma spectrometer to measure the in situ gamma dose rate. The detector is in the upper hole that remains after collecting the sample for luminescence dating, and the results of the measurement are being displayed and stored in the yellow and grey unit at the bottom of the picture

proportion. All of the chemical and emission counting methods described above are applied to subsamples returned to the laboratory for testing. These are from the location of the sample. They will give an accurate assessment of the dose rate provided that they are representative of the materials around the sample. The short range that alpha and beta particles can travel means that material from the sample collected for luminescence measurement will be appropriate. However, gamma rays may travel up to 30 cm in sediment. If the characteristics of the material surrounding the sample vary over this scale, then it is either necessary to take multiple subsamples in the field to characterize these variations or to make measurements of the gamma dose in the field in situ. Field measurements can be made using a portable gamma spectrometer (Fig. 8). These portable systems do not have the energy resolution that is achieved by laboratory-based gamma spectrometry, and so it is not possible to identify emissions from a large number of isotopes. However, it is possible to assess the U, Th, and K concentrations.

A final issue relating to dose rate is whether the dose that is measured today has remained constant during the period being dated. A primary concern here is whether the decay series of U or Th are in secular equilibrium or not (see “► [Radiation and Radioactivity](#)” and “► [Radiation Dose Rate](#)” for discussion of secular equilibrium). Where disequilibrium is detected in the decay series, it may be possible to correct for this if the nature and timing of the disequilibrium can be determined (Olley et al. 1996). Fortunately disequilibrium is not a common problem provided that geochemically active environments are avoided. Typical environments at greater risk of disequilibrium include organic-rich sediments, samples with evidence of cementation since deposition, and environments at the interface between saline and fresh water.



Fig. 9 Sampling sediments for luminescence dating by hammering a metal tube into a section (Photo: G.A.T. Duller)

Practicalities

Sampling

Sampling is a critical part of the application of luminescence dating. Samples for sediment dating should be collected in a way that ensures that there is no exposure to daylight. A common approach is to clean a sediment face and then hammer an opaque plastic or metal tube (typically 5–7 cm diameter and 20–30 cm length) into the section (Fig. 9). Once in the laboratory, material at each end of the tube which may have briefly been exposed to daylight can be removed. This material can be used for measurement of the dose rate. Material from the middle of the tube can then be used for luminescence analysis and prepared in the manner described below.

At some sites it is not possible to insert tubes, and in this case an alternative method of sampling is to cover the sampling position with a large ($\sim 2 \times 3$ m) sheet of thick black plastic to exclude daylight and then extract a sample while working under the plastic sheet in dim red light conditions (as used in the laboratory).

Sample selection is critical, and if possible samples should be taken at least 30 cm from a major stratigraphic boundary to ensure that the volume from which the gamma dose originates is homogeneous. Where samples have to be taken nearer than 30 cm from a boundary, then measurements should be made of the distance from the sample to the boundary, and a subsample of the adjacent material should be collected so that the dose rate contribution from that material can be calculated.

Sample Preparation

Many of the luminescence signals used for dating are sensitive to light, and all are sensitive to heat. Care needs to be taken during sample preparation to ensure that light exposure is kept to a minimum

and that samples are not unduly heated. Dim red lights similar to those used in photographic laboratories are used to provide room lighting both for sample preparation and luminescence measurement. Most luminescence signals are less strongly affected by light at the red end of the spectrum than at the blue, and the eye retains sufficient sensitivity at these wavelengths to allow safe working conditions.

Sample preparation aims to isolate material suitable for luminescence measurements (Wintle 1997). The majority of luminescence dating applications use either quartz or feldspar as the target for luminescence measurements. If present, it is necessary to remove any organics and any carbonates using hydrogen peroxide (H_2O_2) and hydrochloric acid (HCl). Both reactions are exothermic, and care is needed to ensure that samples are not heated above about 60 °C. The grain size used for luminescence measurements are commonly either fine grains (4–11 μm diameter) or coarse grains (within the range of 90–250 μm). Fine grains are sufficiently small that alpha particles will penetrate the grains completely, while for coarse grains the external ~ 30 –40 μm of the grain surface can be chemically removed using hydrofluoric acid, and this removes the external alpha dose to the grains. Thus, choosing one of these two grain sizes simplifies calculation of the external alpha dose rate. The use of grains between these two sizes is more complex.

When using coarse grains, different mineral phases can be obtained using density separation. Quartz is extracted by isolating material with a density between 2.62 and 2.70 g.cm^{-3} . Some plagioclase feldspar persists through this process but is removed when grains are etched in concentrated hydrofluoric acid to remove the external alpha dose and then re-sieved. Potassium-rich feldspars can be concentrated by isolating grains with a density between 2.58 and 2.53 g.cm^{-3} .

When using fine grains (4–11 μm), density separation is ineffective. It is still possible to chemically isolate quartz by etching grains in hydrofluorosilicic acid (H_2SiF_6) for extended periods of time (typically 1–2 weeks). This will remove feldspars, but not quartz.

After preparation, samples are mounted on steel or aluminum discs about 10 mm in diameter suitable for measurement in instruments built by a number of manufacturers. Fine grains are deposited from suspension in acetone to form a uniform layer covering the entire surface of the disc. Coarse grains are fixed using silicone oil, and this makes it possible to control the proportion of the disc surface that is covered and hence the number of grains on each disc.

Application of Luminescence to Dating

Heated Materials

As luminescence dating has become more established, the number of applications has increased dramatically. The technique was originally developed to date the period of time since pottery had been fired, and this remains an important application (see “► [Luminescence, Pottery and Bricks](#)”). Barnett (2000) undertook an extensive set of analyses of pottery sherds from 18 sites around the United Kingdom that had been assigned a later prehistoric age on the basis of their typology. A total of 135 samples were measured. Of these, 24 had independent age estimates based in part on radiocarbon dating of associated finds and good agreement was found. A much larger suite of samples was also measured, and here the age of the pottery was poorly constrained. The study demonstrated the value of luminescence dating in providing numerical ages for individual pottery sherds. The results were especially valuable where only small fragments of pottery were found, and thus typological distinctions were difficult. An additional application to heated materials has been to dating when bricks were fired. This has been extensively applied to medieval buildings across northwestern Europe and is now being applied further afield. Bailiff et al. (2013) applied OSL to date



Fig. 10 Linear dune in the northern Namib Sand Sea. A series of nine boreholes were drilled along a 500 m transect across the dune to collect samples for OSL dating. Vehicles provide the scale (Photo: G.A.T. Duller)

bricks from domed stupas in Sri Lanka, providing some of the first numerical ages for these important archaeological features.

Pottery and bricks are deliberately fired during their manufacture, but other materials may be inadvertently heated and thus dated using luminescence. This is especially useful at Paleolithic sites where fires were lit. Stone tools, especially those manufactured from flint, cannot normally be dated using luminescence methods, but at some sites a small proportion of tools may have been inadvertently heated and this resets the luminescence signal, making it possible to date the occupation (see “► [Luminescence, Flints and Stones](#)”). This method is proving valuable across a range of sites and has yielded very early ages for Middle Paleolithic tanged tools at the site of Ifri n’Ammar in Morocco, ranging from 83 ± 6 ka to 171 ± 12 ka (Richter et al. 2010). Stones which were not tools but were heated by fires may also be dated using luminescence. These too have provided valuable chronological information, for example, at the site of Blombos in South Africa (Tribolo et al. 2006). Here, luminescence dating of sediments and burnt lithics have provided a chronology extending back to 140 ka for a wide range of Middle Stone Age artifacts including engraved ochres, bone tools, and *Nassarius kraussianus* shell beads that are thought to have been used for personal ornamentation.

Unheated Sediments

In the last three decades, the greatest focus for the application of luminescence dating has been to unheated sediments, where the event being dated is the last exposure to daylight. The method is ideally suited to dating the formation of both coastal and desert dunes because there is normally ample opportunity for the mineral grains to be exposed to daylight prior to deposition. Bristow et al. (2007) collected samples from a transect of boreholes across a linear dune in the northern part of the Namib Sand Sea in order to understand the processes involved in forming the feature and the rates of these processes (Fig. 10). A ground penetrating radar survey was undertaken along the same transect prior to OSL sampling and provided stratigraphic evidence of the pattern of sediment accumulation. This stratigraphic evidence was used to choose the locations of the boreholes and the depths at which samples were collected for OSL dating. The OSL ages demonstrated that this very

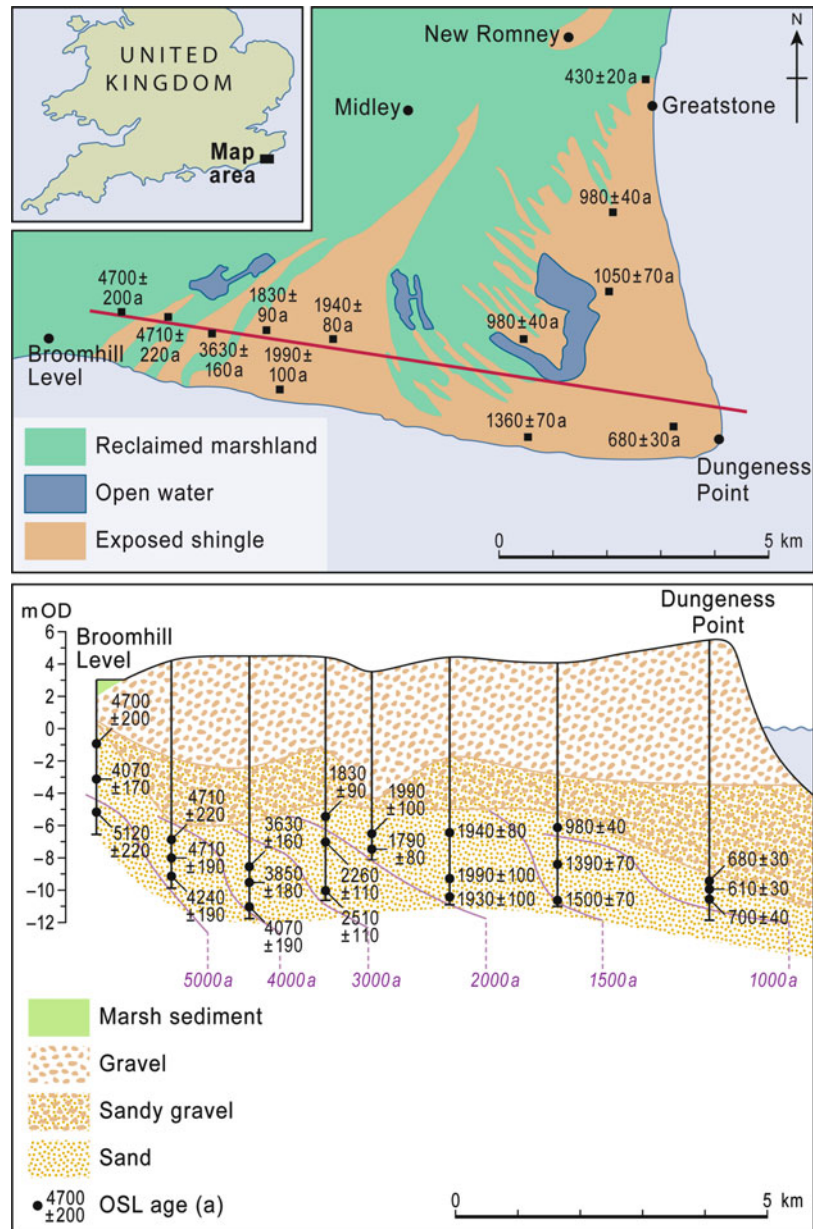


Fig. 11 Dungeness foreland, United Kingdom. The rate of growth of this coastal foreland was determined by applying OSL dating to quartz extracted from sands underlying the gravel ridges that form the surface expression of this feature (Figure adapted from Roberts and Plater 2007)

large dune (~500 m wide and over 60 m high) had been completely reworked within the last 5,700 years and that the flank of the dune had moved 300 m laterally during the last 2,500 years.

Luminescence provides insights into very recent geomorphological events and provides a chronological method that can span both the historic record and the more distant past. Roberts and Plater (2007) used quartz OSL measurements on sands underlying the gravel ridges of Dungeness, a coastal foreland in southern Britain, to provide a rate for the growth of this feature (Fig. 11). Ages for these underlying sands ranged from 430 ± 20 to $5,120 \pm 220$ years, and the younger ages were consistent with documentary historical evidence for growth of Dungeness during the Middle Ages. A number of other impressive data sets utilizing luminescence to provide rates for geomorphological

processes have been produced, including Madsen et al. (2010), who calculated 78 OSL ages for quartz extracted from samples collected from the island of Rømø in the Wadden Sea, Denmark, with beach ridges ranging from 220 ± 20 years ago to over 8,000 years ago. The ability of luminescence dating in these environments to date very recent deposition makes the method ideal for this type of study (see also “► [Luminescence, Geomorphological Processes](#)”).

Limits in the Age Range Dated Using Luminescence

The youngest age that can be obtained using luminescence dating is difficult to define (see “► [Luminescence Dating, Uncertainties and Age Range](#)”). The two major limitations are the extent to which the signal was reset by exposure to daylight at deposition, and the sensitivity of the equipment used to measure the luminescence signal (Madsen and Murray 2009). Ballarini et al. (2003) measured quartz OSL ages for a series of coastal dunes on the island of Texel on the coast of the Netherlands. Maps of this area stretching back 260 years provided excellent independent age control, and the OSL ages were accurate across this entire time period, with one of the youngest samples giving a date of $AD\ 1996 \pm 2$ when it was known to have been deposited between 1996 and 2002 AD. For aeolian and beach sediments where there is extended exposure of grains to sunlight prior to deposition, it is normally possible to obtain accurate ages for samples deposited as recently as the last couple of decades. In fluvial environments it may also be possible to achieve such young ages (e.g., Rustomji and Pietsch 2007), though because of the potential for some grains not to have been exposed to sufficient daylight to completely reset their signal, more complex statistical analysis is normally required (e.g., application of the minimum age model). In environments where the exposure to sunlight is more uncertain (e.g., glacial sediments) or where the luminescence sensitivity of the material is low, the limit for dating may be several hundred to a thousand years.

The upper limit to the age that can be dated using luminescence is also difficult to define. The major controls on this limit are the saturation of the luminescence signal, and the stability of the signal. As quartz or feldspar is exposed to ionizing radiation, the amount of charge trapped within defects increases (Fig. 4). At low doses this increase in trapped charge, and hence in the brightness of the luminescence signal measured in the laboratory, is approximately linear. As exposure to radiation continues, traps within the crystalline material fill, and it becomes increasingly unlikely that charge will be trapped. The result is that the rate of growth of the luminescence signal with radiation dose decreases, until at some point no further increase in luminescence is seen; at this point the luminescence is said to be saturated. Growth of the luminescence signal can be described by Eq. (3) where L_D is the intensity of the luminescence signal at a dose D , L_{Max} is the maximum intensity of the luminescence signal, and D_0 describes the rate at which the luminescence signal approaches saturation:

$$L_D = L_{Max} \left(1 - e^{-\frac{D}{D_0}} \right) \quad (3)$$

As a sample approaches saturation, the uncertainties in the D_e increase, and if the measured natural luminescence signal is within 15 % of the maximum luminescence signal (L_{Max}), then it is normally considered to be beyond the range of luminescence dating methods. This same threshold can also be defined as two times the value of D_0 . The value of D_0 varies from one sample to another, and from one luminescence signal to another. For the OSL signal from quartz, typical values of D_0 are 50–100 Gy, meaning that the maximum value of equivalent dose that can be measured ranges from 100 to 200 Gy. The age range that can be dated in this situation depends upon the dose rate. For

sites where the dose rate is low (e.g., 0.5 Gy/ka), it may be possible to date up to 400 ka, whereas in areas where the dose rate is high (e.g., 4 Gy/ka), then it may only be possible to date as far as 50 ka.

The IRSL signal from feldspar typically has a higher D_0 value than the OSL signal from quartz and so may be able to date older samples. However, potassium-rich feldspars have a significant internal dose from the potassium within the grains, meaning that their total dose rate is higher than that for quartz, so reducing the advantage that they would otherwise have. A great deal of research has been undertaken looking for other luminescence signals, both from quartz and feldspar and from other minerals (e.g., calcite, see “► [Luminescence, Biogenic Carbonates](#)”) that may be able to extend the age range over which luminescence methods can be applied. It still remains to be seen whether these new signals such as Thermally Transferred OSL (TT-OSL) and Violet Stimulated Luminescence (VSL) from quartz, or the TL signal from calcite, will have suitable characteristics for dating.

Novel Applications

Luminescence geochronology has seen rapid development in the last few decades and this rate of progress is continuing. Two exciting new applications of luminescence that have been proposed in recent years are (i) its use in thermochronology and (ii) its use for dating the duration that rock surfaces have been exposed at the Earth’s surface.

Thermochronology (see “► [Thermochronology, Landform Evolution](#)”) attempts to understand the thermal history of a rock and primarily the rate at which it has cooled. Most commonly this is of interest in understanding the rate at which rocks have risen in the Earth’s crust. Luminescence signals can be reset by holding them at high temperatures. Rocks held at high temperatures will not retain charge in defects and thus will not yield any luminescence signal. However, as a rock approaches the Earth’s surface and cools, it will become able to store charge. Thus, rocks that have been rapidly uplifted will yield an apparent luminescence age, and this can be used to yield thermochronological information. Initial work (Herman et al. 2010) used the OSL signal from quartz, and this has an effective closure temperature of 30 °C, far lower than other thermochronometers, thus making new areas of study possible. More recent work has provided a sound theoretical framework for this exciting area (Guralnik et al. 2013), and it seems very likely that this will be a major growth area in the application of luminescence in geochronology.

A second area that has seen recent rapid advances has been the use of luminescence to date rock surfaces (see “► [Luminescence, Rock Surfaces](#)”). Here luminescence is being used to date how long a particular rock surface has been exposed to daylight. Some luminescence signals are reset by exposure to daylight. Commonly these signals are reset rapidly, within periods of seconds to minutes. As daylight penetrates through rock, it is very rapidly attenuated, meaning that while a particular luminescence signal (e.g., the OSL signal from quartz) may be reduced to 0.1 % of its initial signal within a few minutes when exposed to daylight at the Earth’s surface, the OSL signal in samples found a few millimeters inside a rock may take days, years, or millennia to be reset. By drilling a core through the upper few centimeters of a rock and making measurements of the luminescence signal remaining at different depths in the rock, it is possible to build up a picture of how the signal has been reset, and this can be used to determine the duration of time that the rock surface has been exposed (Sohbati et al. 2012).

Further Reading

A simple overview of luminescence dating is provided by Duller (2008b) which is freely available at <http://www.english-heritage.org.uk/publications/luminescence-dating/>. Wintle (2008) gives an excellent overview of the development of luminescence dating in the last half of the twentieth century. Rhodes (2011) provides an excellent overview of the application to dating sediments, while Richter (2007) describes applications to dating burnt flints. Jacobs and Roberts (2007) describe the application of single grain OSL measurements in archaeology. Wintle and Murray (2006) give an excellent review of the application of the single-aliquot regenerative dose (SAR) method applied to quartz.

Cross-References

- Feldspar, Infrared Stimulated Luminescence
- Luminescence Dating, Dose Rate
- Luminescence Dating, History
- Luminescence Dating, Instrumentation
- Luminescence Dating, Single Grain Dose Distribution
- Luminescence Dating, Uncertainties and Age Range
- Luminescence, Coastal Sediments
- Luminescence, Deep Sea Marine and Lacustrine
- Luminescence, Desert Dunes
- Luminescence, Flints and Stones
- Luminescence, Fluvial Sediments
- Luminescence, Geomorphological Processes
- Luminescence, Glacial Sediments
- Luminescence, Pottery and Bricks
- Luminescence, Rock Surfaces
- Quartz Defects, Optically Stimulated Luminescence and Thermoluminescence
- Radiation and Radioactivity
- Radiation Defect
- Radiation Dose Rate
- Radiocarbon Dating
- Terrestrial Cosmogenic Nuclide Dating
- Thermochronology, Landform Evolution

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Luminescence, Biogenic Carbonates

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Definition

Biogenic carbonates. Carbonates, especially calcite and aragonite, precipitated as a result of biological processes.

Luminescence dating. The use of the luminescence signal emitted from a mineral to date its formation or some other event.

Introduction

The emission of luminescence from quartz and feldspar has been widely exploited as the basis for dating sediments, pottery, and burnt stones (see “► [Luminescence Dating](#)”). Calcite (CaCO_3) and its polymorph aragonite yield thermoluminescence (TL) signals which grow with exposure to ionizing radiation in the same way as seen for quartz and feldspar. A number of studies have been undertaken to explore whether geochronological information can be obtained from this TL signal from calcite, and these have focused on trying to date the formation of the mineral. Initial efforts in the 1970s and 1980s (Wintle [1978](#); Debenham and Aitken [1984](#)) studied stalagmitic calcite, but more recently a small number of researchers have looked at the potential of biogenic carbonates, produced by bivalves and molluscs. The TL signal from calcite does not bleach rapidly in light, and dating applications have dated the crystallization event rather than the last exposure to daylight. Nonetheless, it is prudent to minimize light exposure during sampling, preparation, and measurement.

Marine Shells

Shells of the Pectinidae family were shown to give TL signals. Ninagawa et al. ([1992](#)) used this TL signal to determine ages of samples with some independent age control and found that they were able to get ages that were near those expected at several hundred thousand years old but that shells expected to be older than a million years gave underestimates. A major challenge with such work was the presence of organic components within the shell which were intimately intermixed with the calcite structure. To avoid combustion of the organic components within the shells, samples were only heated to a maximum of 240 °C, but even when using a low heating rate (1.7 °C/s), this meant that the measured TL signal may not have had sufficient thermal stability over the long geological periods being studied. Studying a wide range of shellfish, Carmichael et al. ([1994](#)) found that the mineralized component varied from 40 % to 80 % by mass, with the remainder being organic.

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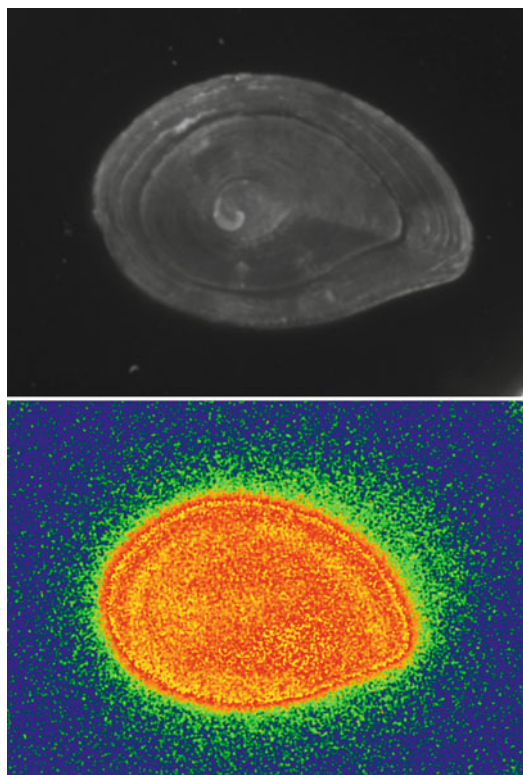


Fig. 1 Operculum of *Bithynia tentaculata*. The operculum is 4 mm across. The *upper image* is taken using a normal microscope, while the *lower image* shows the TL emitted during measurement following a laboratory irradiation. In this *lower image*, *blue* represents low intensity TL emission, while *green*, *yellow*, and *red* indicate increasing intensity (Photos: G.A.T. Duller)

Terrestrial Molluscs

Two other types of biogenic carbonates have received attention in recent years: slug plates and snail opercula (Duller et al. 2009; Stirling et al. 2012). Slugs of the Limacidae family secrete a small plate of calcite, about 2–3 mm in diameter and 0.2 mm thick, enclosed by their mantle. Snails commonly use an operculum to protect themselves and prevent excessive loss of moisture. In many species this operculum is highly organic, but it is highly mineralized in the species *Bithynia tentaculata* (Fig. 1). These two target materials have been shown to yield intense TL signals that grow with radiation to doses over 6,000 Gy. The methods are still experimental but potentially could be used to date the whole of the Quaternary period (2.58 Ma).

Conclusions

Biogenic carbonates, especially calcite, have very great potential for providing geochronological information over the entire Quaternary period. In comparison with other materials used for luminescence dating, they have the advantage that the event being dated is crystallization, and thus, there are no uncertainties about whether the signal was reset at the time of deposition as may occur when

dating sediments or analyzing heated materials. A number of challenges remain to be resolved before the full potential of biogenic carbonates can be realized, including improving the accuracy with which the dose rate can be determined and most critically comparing the results of these new methods with robust independent chronometers.

Cross-References

► [Luminescence Dating](#)

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Luminescence Dating, Loess

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Synonyms

Infrared stimulated luminescence (IRSL); Optical dating; Optically stimulated luminescence (OSL); Thermoluminescence (TL)

Definition

Luminescence dating. A family of chronologic methods typically applied to the commonly occurring minerals quartz and feldspar, which exploits a time-dependent signal that builds up in mineral grains by exposure to naturally occurring ionizing radiation (principally from uranium, thorium, and potassium). The methods assess the time elapsed since these mineral grains were last exposed to sunlight or to heating. In the case of sediments, the event being dated is the last exposure to sunlight, i.e., typically the time of deposition of the sediment.

Loess. A fine-grained terrestrial sedimentary deposit derived from wind-blown dust.

Introduction

Loess deposits preserve one of the most detailed and lengthy terrestrial records of Quaternary climate change on Earth; the key to unlocking these records is the development of a chronology. Early chronologies for loess-paleosol sequences were based largely on correlative techniques, comparing variations in paleoenvironmental proxy data, such as particle size, loess/paleosol thicknesses, and magnetic susceptibility records, and where available using other tie points such as paleomagnetic signatures and tephra layers to link various records. A common assumption in such correlative techniques is a continuous and near-constant sediment accumulation rate over time, with no major hiatus. However, recent high-resolution luminescence dating studies (e.g., Antoine et al. 2001; Frechen et al. 2001; Roberts et al. 2001, 2003; Lai and Wintle 2006) demonstrate that sediment accumulation rates can vary considerably both spatially and temporally and that hiatus can occur (e.g., Lu et al. 2006; Stevens et al. 2006; Thiel et al. 2011a) showing that this assumption is not always valid. This has implications for comparisons of terrestrial, ice-core, and marine oxygen isotope records (e.g., Zhou and Shackleton 1999) and emphasizes the importance of establishing independent numerical chronologies where possible. Luminescence dating has played an increasing role in providing such chronologies for loess sequences, from the earliest applications of the technique to terrestrial sediments through to the most recent proposals for new and/or novel luminescence dating methods and signals.

Much of the early work to derive numerical ages from the upper portions of loess sequences used radiocarbon dating, often applied to paleosol units weathered into the loess. In contrast,

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luminescence dating offers the opportunity to date the deposition event directly because it records the last exposure to sunlight of the grains of quartz or feldspar that make up the sedimentary deposit. The family of luminescence dating techniques also extends beyond the limits of radiocarbon dating in most sedimentary environments and does not rely on the discovery of appropriate *in situ* material (e.g., organic matter or snail shells in the case of dating using radiocarbon or amino acid racemization) which may pre- or postdate the deposition event and/or which may be rare in wind-blown sediments. These reasons, coupled with improvements in the accuracy and precision of luminescence dating over the last 15 years, mean that increasingly, luminescence dating is becoming the technique of choice for determining a numerical chronology for eolian deposits including loess.

An excellent general review of luminescence dating is given by Rhodes (2011) and see also the volume “► [Luminescence Dating](#).” Specific reviews of the application of luminescence dating to loess are given by Wintle (1990) and Zöller and Wagner (1990) for thermoluminescence (TL), while Singhvi et al. (2001) consider the dating of loess using both TL and optically stimulated luminescence (OSL), and Roberts (2008) charts the developments of luminescence dating as applied to loess from the earliest days to the most recent developments (including OSL) at the time of publication. There have, however, been some significant advances since the publication of this last review, several of which are mentioned within this encyclopedia entry.

Historical Overview of Luminescence Dating of Loess

Loess was the first terrestrial clastic sediment to which luminescence dating was systematically applied, and loess deposits have remained important both for the development and the application of luminescence dating techniques since the earliest pioneering work was conducted (Wintle 1981, 1982; Wintle and Brunnacker 1982). The fine-grained nature of loess tends to imply long-transport distances prior to deposition, ideal for the effective zeroing of the luminescence signal, which is a fundamental assumption and requirement of luminescence dating. The dominance of silt-sized particles in loess means that it is the 4–11 μm diameter “fine-grain” fraction, which is typically prepared for dating. Most of the published luminescence dating studies of loess, particularly the earlier studies, are based on the “polyminerale fine-grain fraction,” which is thus termed because it is a mixture of both quartz and feldspar minerals of 4–11 μm diameter. More recently, with the establishment of methods to monitor and correct for sensitivity changes during the measurement procedure, and given the faster optical bleaching of the quartz OSL signal (Godfrey-Smith et al. 1988) compared to other luminescence signals, some workers have used extended fluorosilicic acid treatments of several days’ duration to isolate pure quartz of 4–11 μm grain size or to isolate quartz of coarse silt size (35–50 μm) from loess which is more representative of the grain size distribution. Occasionally, relatively coarse grains (>63 μm) from loess deposits, usually of quartz, have been examined using luminescence techniques; coarse grains cannot be transported over long distances, and such deposits are typically associated with the transition between deposits of sand (source-proximal deposits) and loess (more distal deposits). Use of the 4–11 μm fine-grain fraction or the hydrofluoric acid-etched >63 μm coarse-grained fraction circumvents the need for complex dosimetry assessments of the alpha and beta dose to the sample that are otherwise required when working with intermediate grain sizes (i.e., 11–63 μm).

The earliest luminescence works published on loess were conducted using thermoluminescence (TL) of polyminerale fine grains. Here, the TL is dominated by the signal from feldspars, although the quartz grains present do also contribute to the TL signal; the relative contributions of these two mineral groups are likely to vary between samples due to changes in mineralogy, and it is not always

clear in TL measurements which mineral is being analyzed. Another concern identified in TL dating is the long daylight exposure times (several hours) required to reset the TL signal to a low level at deposition and the fact that an unbleachable residual TL signal remains after this time. This is of particular significance for young material, e.g., of Holocene age, as it could lead to age overestimation; Berger (1987) showed that modern silt could yield an apparent TL age of ~1 ka, and TL ages determined in a study of Japanese loess by Watanuki and Tsukamoto (2001) overestimated the tephra-derived age of the early Holocene and last glacial sediments by more than 10 and 5 ka, respectively.

Thermoluminescence remained the only signal used for luminescence dating of sediments until the development of optically stimulated luminescence signals for dating. Initially, costly Ar-ion lasers (514 nm) were used to stimulate an optical signal from quartz and feldspar (Huntley et al. 1985), and then shortly afterward much less expensive light sources were used to give an infrared stimulated luminescence (IRSL) signal (880 nm) from feldspar (Hütt et al. 1988). Later still, halogen lamp systems and then green and then blue light-emitting diodes (LEDs) were used for optical stimulation and made the study of OSL signals from quartz more practical on financial grounds than the argon-ion laser that was initially used. Use of an OSL signal for dating sediments has the advantage over TL signals since OSL signals are bleached more rapidly and typically to a lower residual level than the TL signal. For these various reasons, the IRSL signal grew in popularity through the 1990s for dating loess, typically applied to polymineral fine grains. During this time, it was not uncommon to see studies generating and comparing both TL and IRSL ages from loess and also comparing the ages generated for these signals using different methods of measurement (e.g., regenerative dose and additive dose, multiple aliquot methods) too. At this time, there was no clear consensus on the luminescence signal or measurement method which gave rise to the most accurate and precise luminescence ages for loess or for other sediments.

One problem which potentially affected both TL and IRSL signals from feldspars is the phenomenon of “anomalous fading” (Wintle 1973), whereby the loss of unstable charge over time leads to underestimation of the true age of deposition if it is not (or cannot be) corrected. Some authors suggest that anomalous fading of luminescence signals from feldspar is a ubiquitous phenomenon (e.g., Huntley and Lamothe 2001; Little et al. 2002), while others find no significant evidence for anomalous fading in their studies (e.g., Frechen and Dodonov 1998; Frechen et al. 2001), and some other authors using feldspars do not consider it at all in their studies. There is no consensus on the most appropriate method for assessing anomalous fading nor for correcting it if it is detected.

Dating using quartz avoids the problems and uncertainties associated with feldspars because the OSL signal from quartz does not suffer from anomalous fading. However, only since the introduction of the single-aliquot regenerative-dose (SAR) measurement procedure of Murray and Wintle (2000) for dating quartz has the quartz component of loess been systematically examined. The SAR procedure brought about a step change in the accuracy and precision of luminescence dating of quartz and successfully addressed the key impediment to the earlier use of quartz for dating loess, namely, monitoring and correcting for sensitivity change which occurs either during the measurement procedure as a result of thermal pretreatments or during burial of the sample. Since this advance, there have been numerous successful applications of luminescence dating using SAR methods applied to quartz from loess, but the upper age limit of this OSL signal is relatively restricted in loess compared to other sedimentary deposits due to the high dose rate of these fine-grained deposits. An upper limit for quartz OSL ages from loess of ~50–70 ka has been reported by several authors (e.g., Zhou and Shackleton 2001; Buylaert et al. 2007, 2008; Lai 2010), although older ages have been reported by others. Feldspars therefore remained potentially attractive for luminescence dating because they saturate at higher values of equivalent dose (D_e) than quartz and

hence potentially extend the upper age limit of dating; however, feldspar methods were still troubled by the specter of anomalous fading.

A major breakthrough came in 2008 when Thomsen et al. reported that the IRSL signal observed at temperature of 225 °C following a prior IR stimulation at 50 °C was much more stable than the conventional IRSL signal that had been previously commonly used, measured at 50 °C. Use of this and other elevated temperature “post-IR IRSL” signals from feldspars potentially offered a means of minimizing or even overcoming the phenomenon of anomalous fading and quickly gave rise to methods which were applied to and tested on loess deposits (e.g., Thiel et al. 2011b; Li and Li 2011; Roberts 2012), extending the upper age limit far beyond that of quartz OSL to ~200–300 ka in loess (e.g., Buylaert et al. 2012; Li and Li 2012). Work to test and validate these post-IR IRSL signals continues, but the various methods proposed show great promise (e.g., see review by Buylaert et al. 2012), and the work of Thomsen et al. (2008) potentially marks the beginning of a revolution in feldspar dating similar to that which occurred in quartz dating following the proposal of the SAR measurement protocol by Murray and Wintle (2000).

Applications of Luminescence Dating of Loess

Loess deposits have played an important role in the reconstruction of long-term climatic and paleoenvironmental change and in correlations between the terrestrial and marine record. These correlations have often been done in the past by wiggle-matching of proxy records, but increasingly where possible, these records are being linked using independently derived absolute or numerical age control in order to explore whether such records are synchronous between sites and to facilitate the potential investigation of leads and lags within paleoclimate and paleoenvironmental systems. Although the uncertainty associated with an individual luminescence age can be relatively large (typically ~5–10 %), where numerous ages are available, these uncertainties can be reduced using Bayesian age-depth models which exploit the information regarding the relative sequence of ages down-section (e.g., Muhs et al. 2013). The ability of luminescence techniques to generate numerical ages relating directly to the deposition event, and the fact that the methods are applied directly to mineral grains which can be found continuously throughout the loess-paleosol sequence, means that there have been very many applications of luminescence dating of loess relating to paleoenvironmental or paleoclimatic reconstruction. For example, paleoprecipitation (e.g., Rao et al. 2013) and paleotemperature (e.g., Jia et al. 2013) records have been reconstructed on a numerical timescale, and changing pressure gradients have been inferred (e.g., Muhs et al. 2013), as have wind-strength fluctuations, and wind directions, and changes in the monsoon intensity (e.g., Maher and Hu 2006; Stevens et al. 2008). The influence of soil-forming durations on the development of mineral magnetic signatures has also been investigated, using luminescence ages to constrain maximum soil-forming durations by dating the loess units that bracket various paleosols (e.g., Maher et al. 2003).

One of the applications which has grown in importance in recent years is the use of luminescence dating applied to loess sequences to assess the magnitude and changes in dust mass accumulation rates (MARs) over time, measured in $\text{g/m}^2/\text{a}$. Through this work, the traditional view of a constant and linear sediment accumulation rate over time, with no major hiatus occurring in the sedimentary record, has been challenged. Loess deposits were also traditionally viewed as a passive record of past climate change, but increasingly the wind-blown dust that the loess deposits are comprised of is being viewed as a potential *agent* of climate change capable of regional modification of climate and is now being incorporated into some climate models (e.g., Mahowald et al. 2006). Luminescence dating has helped to provide some of the first empirical evidence for this potential for regional modification of climate by dust (e.g., Roberts et al. 2003), and critically luminescence-derived

chronologies underpin several of the high-resolution terrestrial MAR determinations which are providing key inputs to the dust component of climate models (e.g., Albani et al. (2014)).

Current Challenges in Luminescence Dating of Loess

The two key challenges posed in the application of luminescence dating to loess both concern the upper limit of dating using luminescence signals. The first key challenge is recognizing and defining the reliable upper age limit for each of the signals within the family of luminescence dating techniques. For example, OSL signals have been observed to grow in the laboratory far beyond what has been described as a prudent upper limit for dating (i.e., beyond 85 % of the maximum achievable luminescence signal when fitted with a single-saturating exponential function). The reliability of OSL ages beyond this range, particularly when obtained using an additional linear component or a second saturating exponential function, is not clearly established, and the origin of this additional component or second saturating exponential function is not understood. Recent work by Chapot et al. (2012) proposed the comparison of laboratory-generated dose-response curves and a “natural dose-response curve” generated using loess samples of known age taken from the Luochuan section of the Chinese Loess Plateau. This work represents the first clear demonstration that OSL ages can increasingly underestimate the true age of the deposits long before the luminescence signal is saturated, and finds the upper limit of reliable dating at this site to be consistent with (although derived in a totally different way to) the upper limits described by others and discussed earlier in this entry. This novel approach of comparing the response in the laboratory and in nature can also potentially be used to investigate the upper limit of dating using other luminescence signals and measurement protocols and is only made possible due to the long record and stratigraphic framework offered by the loess-paleosol sequence studied.

The second key challenge is to seek new methods and signals which might potentially extend the upper limit(s) of luminescence dating, particularly given the long temporal records preserved in many loess deposits. The situation is exaggerated for loess sediments in particular because the environmental dose rate (Gy/ka) is high compared to many other sedimentary deposits, due in part to its fine-grained size and hence large surface area-to-volume ratio. This high dose rate (commonly ~3.5–5 Gy/ka, i.e., ~2–3 times greater than dose rates typically observed in other deposits) means that the minerals within loess deposits are not capable of extending as far back in time (ka) as they can in other sediments even though the total amount of trapped charge (Gy) can be the same. Several methods of extending the age range of luminescence dating have been proposed and are still being explored, including thermally transferred optically stimulated luminescence (TT-OSL; Wang et al. 2006), which was first developed and applied to loess, and use of the violet stimulated luminescence (VSL) signal which may potentially extend the dating range of quartz to span the entire Quaternary period (Ankjærgaard et al. 2013). However, while these new methods are potentially very exciting, they are in the early stages of development, and much remains to be done to demonstrate their ability to generate reliable numerical ages.

Summary and Conclusions

Loess deposits have played, and continue to play, a critical role in the development of luminescence dating techniques. In turn, chronologies derived using luminescence dating techniques are playing an increasingly significant role in deciphering the long and quasi-continuous record of paleoenvironmental and paleoclimatic change preserved within these temporally and areally extensive deposits of wind-blown dust.

Cross-References

- [Feldspar](#)
- [Luminescence Dating](#)
- [Luminescence Dating, Desert Dunes](#)
- [Luminescence Dating, History](#)
- [Luminescence Dating, Uncertainties and Age Range](#)
- [Magnetostatigraphic Dating](#)
- [Paleosol](#)
- [Quartz](#)
- [Radiation Dose Rate](#)
- [Radiocarbon, Terrestrial Carbonates](#)
- [Sediments, Terrestrial \(Palaeomagnetism\)](#)

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Marine Isotope Stratigraphy

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Definition

Marine isotope stratigraphy is the application of proxies of seawater isotopic composition, as preserved in marine sediments and sedimentary rocks, for correlation and dating purposes.

Introduction

Chemical stratigraphy, or chemostratigraphy, is the application of chemical signatures preserved in sediments and sedimentary rocks for the purpose of correlation, dating, or interpreting past environments and environmental change (Weissert et al. 2008; Halverson et al. 2010). Marine isotope stratigraphy is the most important subdivision of chemostratigraphy and encapsulates diverse stable and radiogenic isotope systems that have been applied to studies of marine strata spanning from Archean to Recent in age. The list of isotope systems that have been investigated is large and growing, spurred in part by significant recent developments in gas source (IRMS) and multi-collector inductively coupled plasma (MC-ICP-MS) mass spectrometry (see also entry on ► [Mass Spectrometry](#)). However, the focus here is on a small subset of established isotope proxies that are widely utilized and particularly useful for chronostratigraphic purposes. Specifically, the light stable isotope systems of oxygen ($\delta^{18}\text{O}$), carbon ($\delta^{13}\text{C}$), and sulfur ($\delta^{34}\text{S}$) and the radiogenic isotope systems of neodymium ($^{143}\text{Nd}/^{144}\text{Nd}$), strontium ($^{87}\text{Sr}/^{86}\text{Sr}$), and osmium ($^{187}\text{Os}/^{188}\text{Os}$) are briefly reviewed.

Underlying Principles

An overarching principle in the application of marine isotope stratigraphy is that targeted materials for analysis, such as shells or organic matter in marine sediments, can be regarded as reliable proxies of the isotopic composition of the seawater in which they formed. Where these data are to be applied for correlation or dating, it is paramount that the residence time of the isotope system in seawater is sufficiently large relative to the mixing time of the oceans ($\sim 10^3$ years) that the isotope proxy retains a global seawater signature. If these conditions are met and the isotope systems have not been significantly disturbed by subsequent diagenesis or other alteration, then fluctuations, or in some cases absolute values, in the isotope ratios can be used to correlate strata deposited in different parts of the global ocean or assign an approximate age based on comparison with a reference marine isotope curve (see also entry on ► [Seawater Sr Curve](#)). Because seawater compositions of most commonly applied isotope ratios have varied secularly over Earth history,

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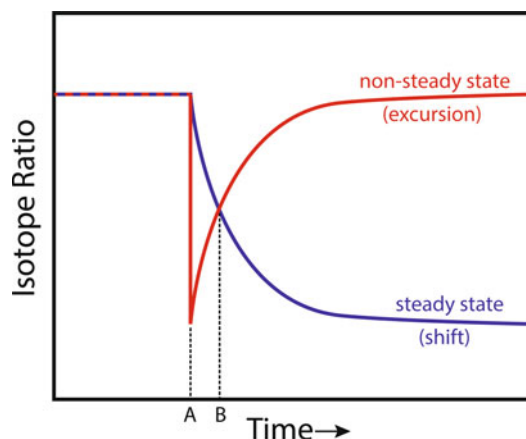


Fig. 1 Schematic illustration of the difference between steady-state and non-steady-state changes in marine isotope ratios. A steady-state shift (*blue line*) results from a change in the isotope ratio of the input to or output from the ocean of a given system. For example, a shift in $^{87}\text{Sr}/^{86}\text{Sr}$ could result from the extrusion of a large continental flood basalt (*time A*) and resulting decrease in average weathering input. The timescale over which the shift occurs is proportional to the residence time of that element in the ocean. A non-steady-state perturbation (*red line*) results in an *excursion*, commonly driven by a relatively rapid input of the element of interest to the ocean reservoir (at *time A*), such as a catastrophic release of low $\delta^{13}\text{C}$ methane from seafloor clathrate reservoirs. The magnitude of the excursion is a measure of the relative size of the non-steady-state addition (or subtraction) of the element to seawater, and the timescale over which the system recovers is governed by the residence time.

a simple isotope ratio or profile is typically insufficient to assign an age, and other chronostratigraphic tools, such as biostratigraphy, magnetostratigraphy, or absolute ages on bounding strata, must be used first to narrow down the possible age range of a given sample or stratigraphic section. The most useful proxies and time intervals in which they are applied are those that show rapid changes in seawater composition (McArthur et al. 2012). Fortuitously, isotopic shifts and excursions (Fig. 1) are common across major geological events, such as mass extinctions, glaciations, and episodes of abrupt warming.

Stable Isotopes

Temporal fluctuations in stable isotope compositions of seawater result from the tendency of isotopes to fractionate at low temperatures due to their relative mass differences. These mass discrepancies give rise to subtle but important differences in the strength of chemical bonds formed in molecules by the different isotopes of a given element. The result is the preferential diffusion, reaction, or biological uptake of one isotope over another, resulting in fractionation of isotope ratios between different molecules or phases. This fractionation generates geological or oceanic reservoirs with contrasting isotopic ratios. For example, the exit channels of carbon from the seawater dissolved inorganic carbon (DIC) pool can be subdivided into inorganic (i.e., carbonate; relatively ^{13}C enriched) and organic sedimentary carbon (^{13}C -depleted) sinks. The relative importance of these sinks controls the $^{13}\text{C}/^{12}\text{C}$ ratio of the DIC pool at steady state.

Many biogeochemical and geological processes can drive the secular variation in isotope ratios in seawater, but those changes that occur at timescales useful in stratigraphy are commonly the result of changing paleoenvironments. Where these changes occur at steady state (i.e., the mass of the seawater reservoir of the element of interest does not change in time), the resulting isotopic change is gradual. However, the most useful isotopic fluctuations are commonly in the form of relatively brief *excursions* (Fig. 1) that result from sudden or catastrophic events, such as glaciation (see section on oxygen isotopes below), flood basalt volcanism, and mass extinctions. Such events

often give rise to precipitous (non-steady state) changes in multiple isotope proxies simultaneously (e.g., fluctuations in carbon and oxygen isotope ratios are commonly correlated or anticorrelated). Importantly, the timescale of these changes may differ due to variable oceanic residence times and the proximal driving mechanism for the perturbation.

Radiogenic Isotopes

Variations in the ratios of radiogenic isotopes in seawater are fundamentally the result of the fractionation of two elements that include the parent and daughter isotopes of a given radiogenic system (e.g., Rb and Sr, where ^{87}Rb decays to ^{87}Sr) between geological reservoirs, rather than isotopic fractionation. Coupled with progressive decay of the radiogenic isotope, this elemental fractionation produces reservoirs, such as the mantle and the continental crust, with distinct radiogenic isotope fingerprints. Progressive decay of the radiogenic isotope results in a first-order, long-term rise in the radiogenic isotope ratio over Earth history. Changes in the relative weight of the flux to the ocean of one of these elements from the different reservoirs result in a steady-state *shift* in the isotope ratio in seawater, over a timescale determined by the residence time of that element in seawater (Fig. 1), and the time span over which the change in flux occurs. In some cases, sharp excursions may occur.

Development and Application of the Method

The origin of marine isotope stratigraphy can be traced to the pioneering work of Harold Urey and his research group at the University of Chicago in the 1950s who analyzed carbon and oxygen isotope ratios in modern and ancient carbonate shells and other biogenic materials. The initial motivation of Urey's group was in reconstructing paleoenvironments, namely, past seawater temperatures (Epstein et al. 1951; Urey et al. 1951). However, Emiliani's (1955) documentation of systematic stratigraphic (hence, temporal) variations in oxygen isotope ratios in foraminifera tests recovered from Pleistocene sediment cores established the great potential of oxygen isotope stratigraphy for correlation and dating purposes (Emiliani 1958). Oxygen isotopes would subsequently prove to be an invaluable and much more effective means of reconstructing the tempo and magnitude of late Cenozoic glacial advances and retreats than the continental record of glacial drift (e.g., Shackleton and Opdyke 1973; Hays et al. 1976; Lisiecki and Raymo 2005).

Although Wickman (1948) first speculated that strontium isotopes were a potentially useful dating tool in marine carbonates and evaporites well before analytical techniques became routine, the full potential of strontium isotope stratigraphy was not realized until Burke et al. (1982) published the hallmark record of Phanerozoic seawater Sr isotope compositions, which demonstrated substantial variations in $^{87}\text{Sr}/^{86}\text{Sr}$. Similarly, carbon isotope stratigraphy did not emerge as an effective and efficient chronostratigraphic tool until the late 1970s and early 1980s (e.g., Berger et al. 1978; Scholle and Arthur 1980), but is now a standard technique when working on sedimentary carbonates of all ages.

Stable Isotope Systems

Due to the relatively small absolute variations in stable isotope ratios, such as $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$, most commonly measured stable isotope ratios are expressed as per mil (parts per thousand) units in delta (δ) notation, relative to an international standard:

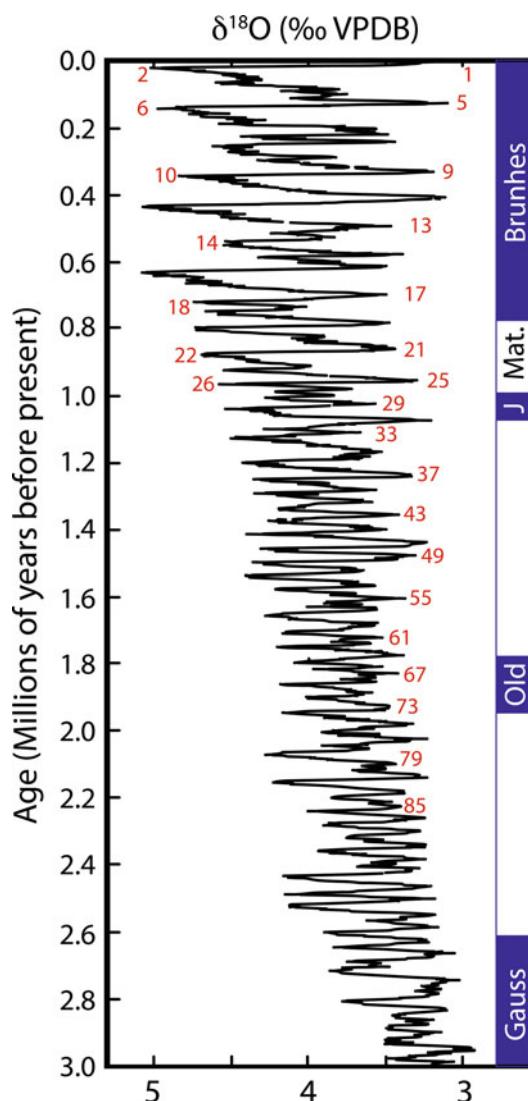


Fig. 2 The benthic foraminifera oxygen isotope record (LR04) for the past three billion years, as compiled by Lisiecki and Raymo (2005) from a stack of 57 sediment core records. Note that even-numbered stages correspond to glacial maxima and odd-numbered stages to glacial minima. Red numbers refer to *marine isotope stages (MIS)*, although note that only selected stages are labeled. Glacial maxima occur at higher $\delta^{18}\text{O}$ values (positive MIS; see text for explanation), hence the inverse values on the x -axis. The boxes on the right delineate normal (blue) and reversed (white) magnetic polarity chrons. *Mat.* Matuyama, *J* Jaramillo, *Old* Olduvai.

$$\delta (U_{\text{wasyh}}) = 1000 \times \left(\frac{R_{\text{SAM}} - R_{\text{STD}}}{R_{\text{STD}}} \right)$$

where R_{SAM} and R_{STD} refer to the isotope ratio of interest of a measured sample and standard, respectively. Many different isotope ratios are measured on sediments and sedimentary rocks, but of these, few have proven consistently effective in chronostratigraphy. Several other systems have very specific environmental applications, such as boron isotopes (paleo-pH) and clumped C–O isotopes (paleo-temperature) in carbonates. Other proxies, such as Mg, Ca, and Li isotopes in carbonates, have emerged as potentially useful chemostratigraphic tools, but are either not yet well established or are not effective replacements for established isotope systems.

Oxygen Isotopes

Oxygen isotope stratigraphy has proven invaluable in understanding Cenozoic paleoclimate (Emiliani 1958; Hays et al. 1978; Zachos et al. 2001; Lisiecki and Raymo 2005) and has enjoyed wide application to rocks and sediments of all ages. Oxygen isotope ratios are normalized to two different standards: PDB (named for belemnites in the Cretaceous Peedee Formation, which was the original laboratory carbonate standard developed by Urey's group at the University of Chicago, and subsequently recalibrated as VPDB) and SMOW (Standard Mean Ocean Water standard, recalibrated as VSMOW). Oxygen isotope values for a given material can be converted between these two standardizations using the equation

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \times \delta^{18}\text{O}_{\text{VPDB}} + 30.91$$

By convention, silicate and phosphate minerals are standardized to VSMOW and carbonate minerals are standardized to VPDB. Here, we are only concerned with those minerals deposited from seawater, most importantly aragonite and calcite, although oxygen in phosphate biominerals is also used for chemostratigraphy. The original oxygen isotope composition of these minerals is determined by temperature at which the mineral formed and the $\delta^{18}\text{O}$ of the oxygen source for that mineral, which, in the case of carbonates, is the oxygen bound to carbon in the dissolved inorganic carbon (DIC) pool (Grossman 2012). The $\delta^{18}\text{O}$ of DIC, in turn, is governed by the $\delta^{18}\text{O}$ of seawater. Hence, oxygen isotope ratios can be used as a paleothermometer, assuming the composition of the waters from which the carbonate was precipitated is known (Epstein and Mayeda 1953).

Carbonates are strongly enriched in ^{18}O relative to the waters from which they precipitate. Because this fractionation is controlled by temperature, with larger fractionations occurring at lower temperatures, if seawater composition is held constant, then increasing temperatures result in carbonates with lower $\delta^{18}\text{O}$ values, and vice versa. However, seawater composition does vary, specifically as a consequence of the growth and decay of continental ice sheets, which are strongly depleted in ^{18}O compared to seawater. The magnitude of this shift between the last glacial maximum and today was about 0.9 ‰ (Schrag et al. 1996). Fortunately, this *ice volume effect* drives the $\delta^{18}\text{O}$ of seawater to higher values during glacial maxima and lower values during glacial minima – that is, in the same direction as the temperature effect. Hence, oxygen isotopes are invaluable in reconstructing late Cenozoic (Pliocene–Pleistocene) glaciation, which is now widely accepted to be modulated by orbital (Milankovitch) cycles (Hays et al. 1976). Indeed, both marine carbonate and ice core $\delta^{18}\text{O}$ records over the past five million years are commonly tuned to oscillations in insolation (typically June 21 insolation at 65°N; e.g., Shackleton 2000; Zachos et al. 2001).

Figure 2 shows the marine benthic foraminifera (i.e., deep water) $\delta^{18}\text{O}$ record (LR04) for the past 3 m.y., as compiled and orbitally tuned by Lisiecki and Raymo (2005). Benthic forams are preferred over planktonic forams for generating seawater curves because the latter are sensitive to local temperature or salinity affects, whereas benthic forams better capture whole ocean values and trends. The LR04 record captures many key features, including a general increase in $\delta^{18}\text{O}$ of marine carbonates through the Pliocene–Pleistocene that is presumably related to gradual intensification of continental glaciation; the well-developed, asymmetric sawtooth 100 k.y. glacial–interglacial cycles over the past 800 k.y.; and the prevalence of 40 k.y. glacial cycles prior to 800 k.a. The peaks and troughs in the marine isotope record are identified as numbered marine isotope stages, beginning with the present low (interglacial) stage (MIS 1) and extending back through the Pliocene (Lisiecki and Raymo 2005). Correlating stages between a given oxygen isotope record and the LR04 or other compilation provides a means of dating sediment (or ice) cores and enables

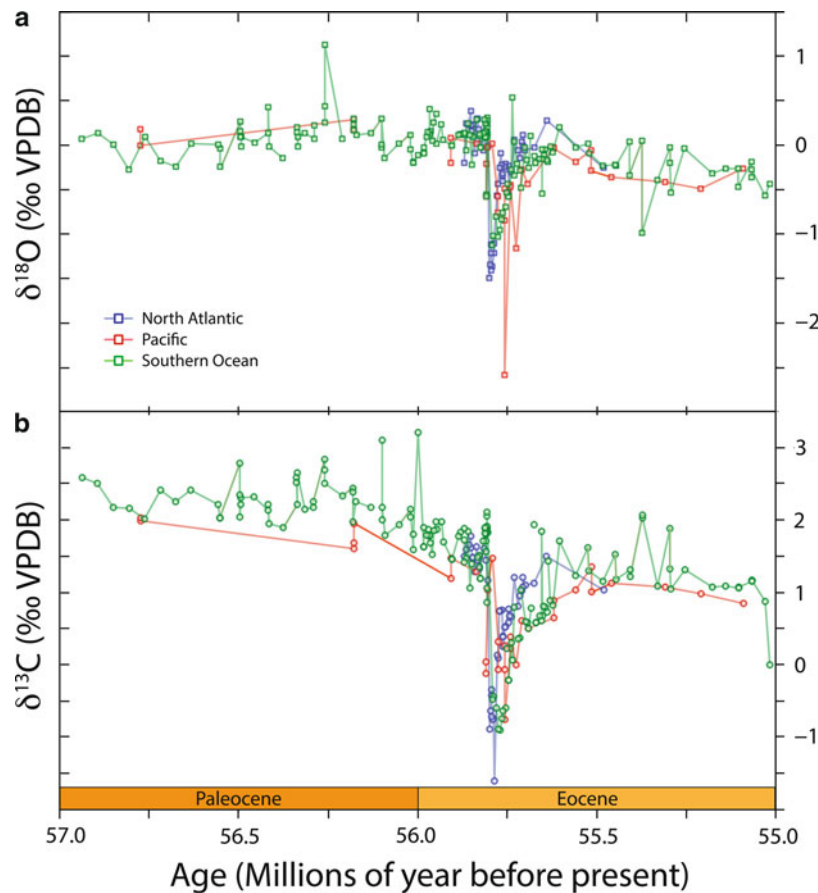


Fig. 3 Compilation of oxygen (a) and carbon (b) isotope data from benthic foraminifera, spanning the Paleocene–Eocene Thermal Maximum (*PETM*) event, which is attributed to a catastrophic input of ^{13}C -depleted carbon to the ocean–atmosphere system (see Zachos et al. (2007) for a review of possible mechanisms and consequences of this event). Carbon and oxygen isotope records (extracted from the database of Cramer et al. 2009) from individual cores from the North Atlantic (ODP1051), Pacific (ODP865), and Southern Oceans (ODP690) are shown for comparison.

direct correlation and comparison of equivalently aged strata, which remains valid even if the timescale of the compilation is subsequently revised. This technique is most reliably applied to deep-sea strata that experience consistent, uninterrupted sedimentation.

Oxygen isotope stratigraphy is also widely applied to older strata and successfully delineates many key climatic events and trends over the Cenozoic Era, including the Paleocene–Eocene Thermal Maximum (Fig. 3a), the onset of Antarctic glaciation (Eocene–Oligocene boundary), and mid-Miocene climatic optimum (Zachos et al. 2001). The utility and reliability of this proxy decreases back in time with diminished deep-sea sediment records and increasing degree of alteration of most carbonate sediments and rocks. Nevertheless, $\delta^{18}\text{O}$ anomalies and trends that are consistent with known events such as glaciations have been documented in rocks spanning the Phanerozoic (Grossman 2012).

Inorganic Carbon Isotopes

The carbon isotope ratio ($^{13}\text{C}/^{12}\text{C}$) of the marine-dissolved inorganic carbon (DIC) pool has varied secularly over Earth history. The steady-state $\delta^{13}\text{C}$ value of DIC reflects the composition of carbon input to the ocean (commonly assumed to be -5‰ to -6‰ over long timescales; Kump and

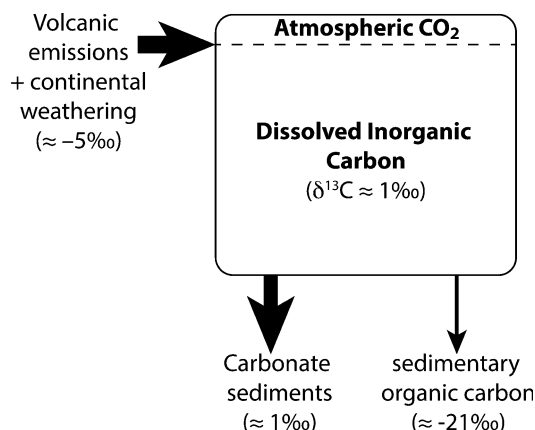


Fig. 4 A simple schematic model of the coupled atmosphere–ocean carbon cycle at present, which illustrates the carbon isotope composition of the major fluxes and reservoirs that affect the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC) in seawater and sedimentary carbon over geological timescales. Steady-state changes in the $\delta^{13}\text{C}$ value of DIC can be effected by (1) a change to the composition of the input to the coupled ocean–atmosphere system, (2) a change in the relative amount of carbon removed from the ocean–atmosphere system and buried in sediments, and (3) the $\delta^{13}\text{C}$ composition of organic carbon. A non-steady excursion can be brought about by a sudden input of isotopically distinct carbon to the DIC–atmosphere reservoir.

Arthur 1999), the relative partitioning of that carbon into inorganic (carbonate; $\delta^{13}\text{C}_{\text{carb}}$) carbon and sedimentary organic carbon ($\delta^{13}\text{C}_{\text{org}}$) that is buried within marine sediments (f_{org} = fraction of carbon buried as organic matter), and the isotopic difference between these two reservoirs ($\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}} \approx \delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{org}}$) (Fig. 4). Because $\delta^{13}\text{C}_{\text{carb}}$ is close to the value of the DIC reservoir and the fractionation between the two species is effectively insensitive to temperature, the carbon isotope composition of marine carbonates is treated as an approximation of seawater from which it derives.

This approximation is most applicable to pelagic carbonates, which are deposited in the open ocean. The predominant sources of pelagic carbonate are calcareous nannoplankton (e.g., Cocolithophora) and planktonic foraminifera. Although these two groups evolved earlier, neither was widespread in the global ocean until the early Cretaceous (Saltzman and Thomas 2012). Consequently, most middle Mesozoic–Cenozoic marine carbon isotope compilations are derived from deep-sea sediment cores. These may be either bulk carbonate records, which dominantly comprise planktonic nannofossils (Milliman 1993), or records developed from individual planktonic or benthic foraminifera (e.g., Fig. 5). Because the DIC of the surface mixed layer may be heavily modified by primary productivity (photosynthesis), planktonic and bulk records may vary considerably from the benthic foraminifera records, which are a more faithful proxy for whole ocean DIC composition. Combined planktonic and benthic foraminifera records may be used to quantify the effect of the biological pump, which produces a surface-to-deep $\delta^{13}\text{C}$ gradient where surface waters are relatively ^{13}C enriched.

Even benthic foraminifera records may not precisely record the carbon isotope composition of the integrated oceanic DIC pool. As shown in Fig. 5, the present Pacific and North Atlantic basins are offset from one another by about 1 ‰. This carbon isotope gradient between the two ocean basins first developed in the middle Miocene. For the remainder of the Cenozoic Period, the North Atlantic and Pacific records align reasonably well, and both capture major shifts in $\delta^{13}\text{C}$, including a large decline across the Paleocene–Eocene boundary (punctuated by the PETM event; see below), the ca. 17 Ma Monterey carbon burial event, and a steady decline starting about 8 million years ago and presumably related to the expansion of C4 plants (Fig. 5; Zachos et al. 2001). Such

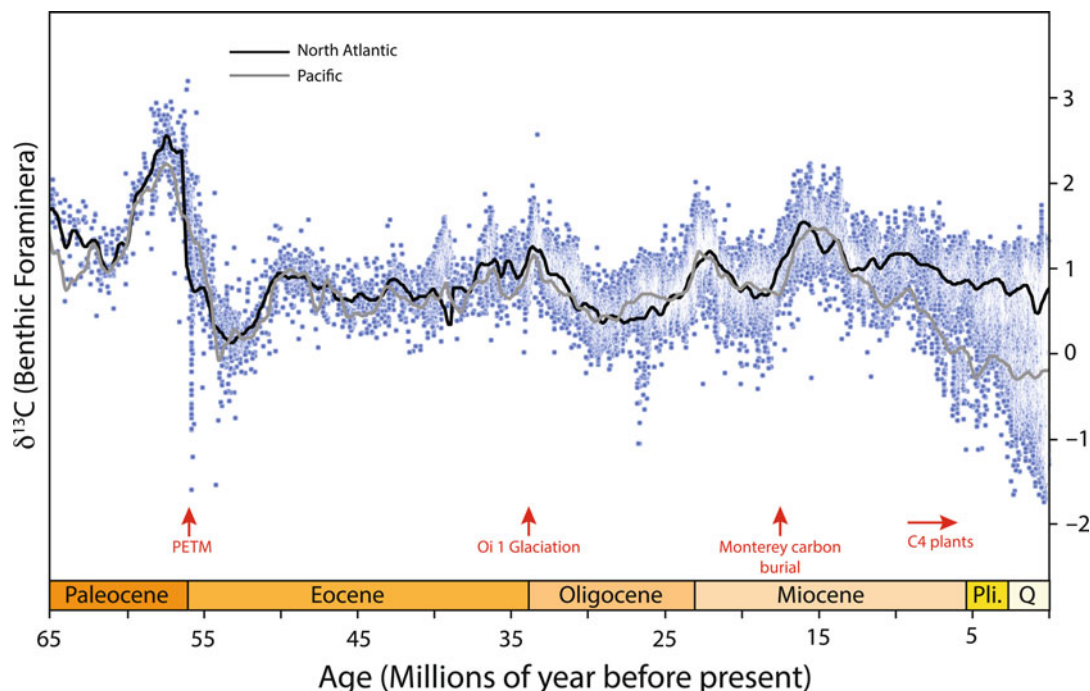


Fig. 5 Compilation of carbon isotope composition of benthic foraminifera over the past 65 million years (Cenozoic). Blue data points represent all data from deep-sea sediment cores, as compiled by Cramer et al. (2009), adjusted to the timescale of Gradstein et al. (2004). White swaths indicate intervals with extensive data coverage. Black and grey lines are fits to the North Atlantic and Pacific data, respectively (Cramer et al. 2009). Several carbon isotopic features are apparent in this curve, including the Paleocene–Eocene Thermal Maximum (PETM) negative excursion (see also Fig. 3), the Monterey Carbon Burial Event, and a decline in marine $\delta^{13}\text{C}$ corresponding to the expansion of C4 plants beginning about eight million years ago (Zachos et al. 2001). Note the gap between Pacific and North Atlantic $\delta^{13}\text{C}$ beginning in the middle Miocene, indicating an increasing isotopic gradient between ocean basins.

salient trends are important from the perspective of chronostratigraphy because they permit correlation and approximate dating of poorly age-constrained sections by comparison with a reference seawater $\delta^{13}\text{C}$ curve. However, because both positive and negative steady-state shifts are relatively common occurrences in the geological record, they typically require additional chronological constraints or a long record with enough structure that it can be confidently correlated to the reference curve.

Non-steady-state perturbations to the seawater DIC isotopic composition, known as *carbon isotope excursions*, may provide a unique solution when correlating and dating marine sediments. Perhaps the best-studied example of such a non-steady-state excursion is the carbon isotope anomaly that spans the Paleocene–Eocene Thermal Maximum (PETM) (Fig. 3). This anomaly features an abrupt decline in the $\delta^{13}\text{C}$ composition of benthic foraminifera of 2–3 ‰, followed by a gradual recovery over a few hundreds of thousands of years (Fig. 3b); this timescale is governed by the c. 100–200 thousand-year residence time of DIC in the oceans. It is widely accepted that this excursion must have resulted from the geologically instantaneous addition of a large mass of ^{13}C -depleted carbon to the marine DIC pool. However, the actual source of this carbon and its precise link to the corresponding temperature change evinced by the oxygen isotope record (Fig. 3a) remain debated (Higgins and Schrag 2006).

Carbonates deposited on continental margins tend to show greater variability than pelagic carbonate records. One reason for this discrepancy in signals is that they are more susceptible to local and regional affects that generate heterogeneity in seawater DIC, such as input of ^{13}C -

depleted surface and groundwater or elevated bioproductivity and removal of ^{13}C -depleted organic matter. This problem is particularly acute in restricted water bodies, such as epeiric seas, where local carbon cycling processes can strongly influence the $\delta^{13}\text{C}$ record preserved in carbonate sediments (e.g., Holmden et al. 1998; Panchuk et al. 2005). Another reason for the variability is that platform carbonates are more susceptible to overprinting by meteoric diagenesis, particularly during glacial epochs where they are periodically exposed during glacioeustatic lowstands (Swart 2008). Nevertheless, because deep-sea pelagic carbonates are absent from the pre-Mesozoic record and other deepwater records are sparse, carbon isotope stratigraphy is heavily dependent on records derived from shallow-water carbonate platforms (Saltzman and Thomas 2012). The reliability of these archives for chemical stratigraphy remains highly debated (Derry 2010).

Organic Carbon Isotopes

The carbon isotopic composition of marine sedimentary organic matters ($\delta^{13}\text{C}_{\text{org}}$) also yields important paleoenvironmental information and in some cases is a useful chemical stratigraphic tool. Most carbon isotope data produced on sediments and sedimentary rocks are measured on bulk total organic carbon (TOC). To the extent that this TOC reservoir is largely derived from primary biomass and has not been heavily altered isotopically during diagenesis and metamorphism, it should closely parallel the original DIC pool from which that carbon was fixed (Hayes et al. 1999). For this reason, the carbon isotopic composition of bulk sedimentary organic carbon ($\delta^{13}\text{C}_{\text{org}} \approx -20$ to -30 ‰) has been widely applied in place of or as a supplement to carbonate carbon isotopes (where carbonate is scarce) to capture secular evolution and excursions in the DIC reservoir (e.g., Knoll et al. 1986).

Paired carbonate and organic carbon data can additionally be used to calculate the net isotopic fractionation between the inorganic and organic carbonate fractionations (ϵ_{TOC}), which is an approximation of the initial fractionation between DIC and the primary (photosynthetic) organic carbon pool (Hayes et al. 1999). This figure can vary considerably due to a several factors, but mainly to differences in the initial fractionation between dissolved CO_2 and primary biomass (ϵ_{p}) which is imparted by primary producers and principally controlled by dissolved CO_2 concentrations, growth rate, and cell geometry (Popp et al. 1998). Not surprisingly, ϵ_{TOC} has varied considerably over geological time, with highs of up to 34 ‰ during the Neoproterozoic (100–541 Ma) and current values below 22 ‰ (Hayes et al. 1999). As a consequence, $\delta^{13}\text{C}_{\text{TOC}}$ cannot simply be used as a replacement for $\delta^{13}\text{C}_{\text{carb}}$, even though it commonly captures the major excursions and trends in the DIC reservoir and hence can be applied to chronostratigraphy.

Sulfur Isotopes

Sulfur isotope stratigraphy has been applied to a wide range of paleoenvironmental questions, for which the ratio $^{34}\text{S}/^{32}\text{S}$ is commonly used. Sulfur occurs in seawater mainly in the oxidized form of sulfate (SO_4^{2-}), but locally and at times in the past has also been abundant in its reduced form of hydrogen sulfide (HS^-). Sulfate is delivered to the ocean mainly through continental weathering ($\delta^{34}\text{S} = 0$ –10 ‰) and removed as both sulfate and sulfide. The sulfate is sequestered in evaporite minerals (gypsum and anhydrite), barite (CaSO_4), and as a trace constituent in carbonate minerals (carbonate associated sulfate), all of which may be used as proxies for seawater sulfate isotopic compositions. Under anoxic conditions, sulfate is also utilized as the electron acceptor during bacterial sulfate reduction (BSR). This metabolic pathway, along with complex redox recycling of intermediate sulfur species, produces sulfide that is depleted in ^{34}S relative to seawater sulfate typically by ~ 30 –60 ‰. The highly variable figure results in a wide range of $\delta^{34}\text{S}_{\text{sulfide}}$ values in the sedimentary record (Canfield 1998). For this reason, $\delta^{34}\text{S}_{\text{sulfide}}$ is not an especially useful tool in

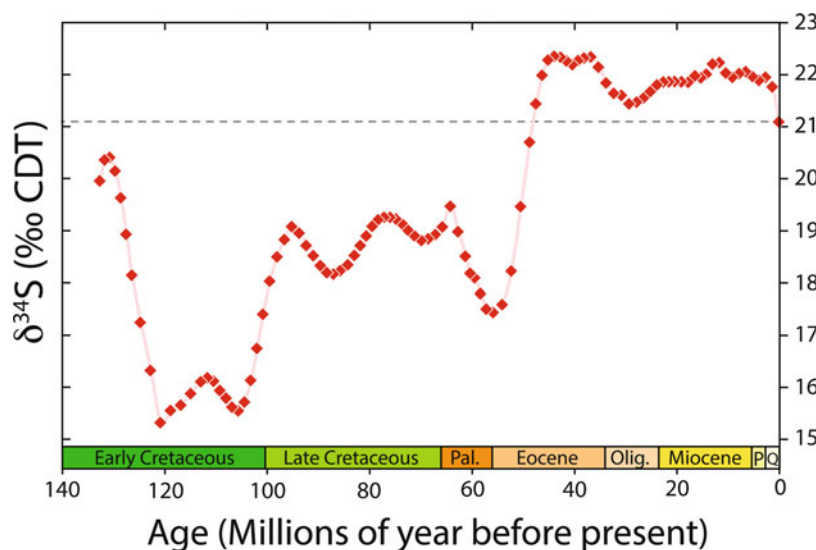


Fig. 6 A LOWESS fit sulfur isotope curve to the marine barite $\delta^{34}\text{S}_{\text{SO}_4}$ record for the past 130 million years (Paytan et al. 2004), modified from Paytan and Gray (2012). Barite, which is a trace constituent in many deep-sea sediments, is presumed to preserve primary seawater sulfate isotope ratios and is a robust during diagenesis, which makes it a well-suited mineral for reconstructing ancient seawater composition.

chronostratigraphy, although distinct ranges in $\delta^{34}\text{S}_{\text{sulfide}}$ are characteristic of certain time intervals over Earth history (e.g., Canfield 1998).

The generally highly depleted values of sedimentary sulfide are responsible for the relatively high $\delta^{34}\text{S}$ of sulfate in seawater. Sulfate is the second most abundant anion (after Cl^-) in modern seawater and has a residence time of nearly ten million years. Hence, sulfate is effectively uniform in the modern ocean ($\delta^{34}\text{S}_{\text{SO}_4} = 21.0 \pm 0.1$ ‰ in modern seawater; Rees et al. 1978), and its isotopic composition is expected to remain relatively stable over timescales of millions of years (Paytan and Gray 2012). Nevertheless, $\delta^{34}\text{S}_{\text{SO}_4}$ has varied considerably over Earth history, in large part as a result of significant changes in the size of the sulfate reservoir and hence its sensitivity to perturbations by changes in other parameters controlling its isotopic composition, namely, the net fractionation accompanying BSR and sulfide burial and the fraction of sulfur buried as sulfide. Due to high intrinsic variability of $\delta^{34}\text{S}_{\text{SO}_4}$ values recorded in pre-Mesozoic sedimentary rocks and difficulty in establishing their fidelity as seawater proxies, sulfur isotope stratigraphy has limited application as a dating tool throughout most of Earth history. However, in some cases, sulfur isotope chemostratigraphy can be used to apply rough age constraints. For example, distinctly ^{34}S -enriched values ($\delta^{34}\text{S}_{\text{SO}_4} > 30$ ‰) characterize the latest Precambrian and Cambrian sulfur isotope record (Kampschulte and Strauss 2004). The sulfur isotope record for the past 130 million years shows many distinct features, notably a 5 ‰ decline between 130 and 120 Ma and a rise of similar magnitude around 55 Ma (Fig. 6; Paytan et al. 2004; Wortmann and Paytan 2012). This unique structure to the seawater $\delta^{34}\text{S}_{\text{SO}_4}$ record presents potential of using sulfur isotopes for age determinations in sedimentary rocks of middle Mesozoic and younger age, although in many cases, other proxies would be more effective.

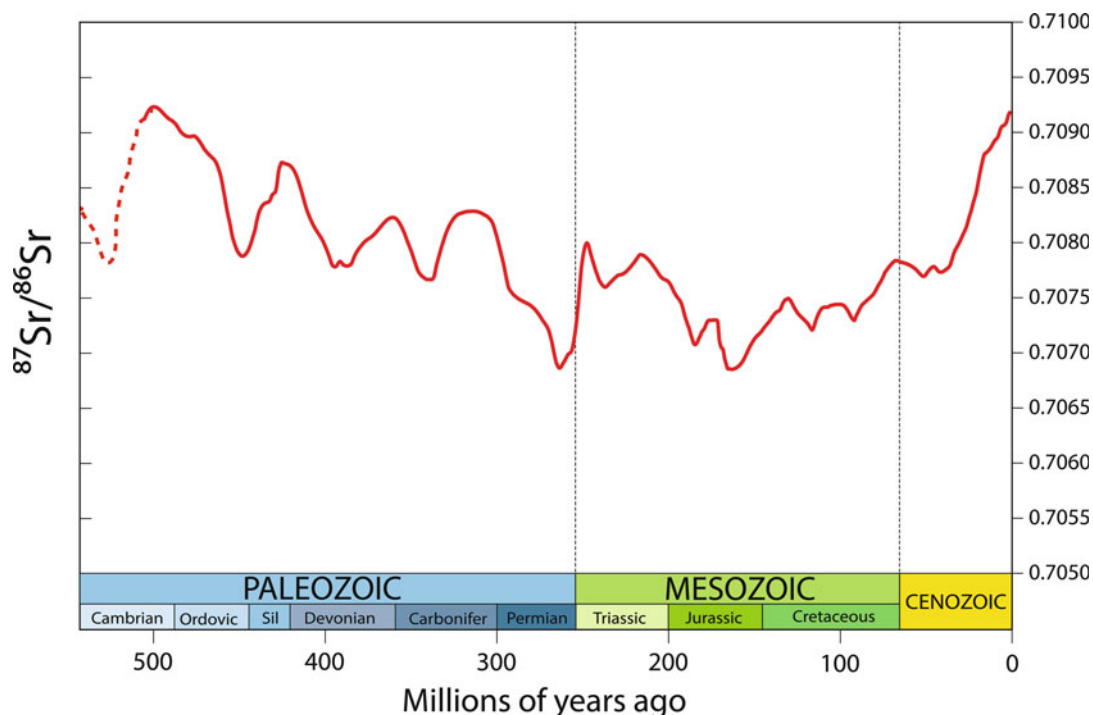


Fig. 7 A LOWESS fit Sr isotope curve for the Ordovician to present (McArthur et al. 2012), plus the Sr isotope fit to data for the Cambrian from Shields and Veizer (2002) and Halverson et al. (2010). See entry on “► Seawater Sr Curve” for a more detailed discussion of this record and its application to chronostratigraphy.

Radiogenic Isotope Systems

In addition to their direction applications in geochronology, several different radiogenic isotopes systems serve as important chemical stratigraphic tools. Although many different radiogenic isotope systems have been applied to marine sedimentary records for multiple purposes, only a limited number of these techniques enjoy routine application with chronostratigraphic relevance. Radiogenic isotope ratios are conventionally reported with a stable isotope with a radiogenic contribution of a given element as the numerator (e.g., ^{87}Sr) and a stable isotope with no or a negligible radiogenic component as the denominator (e.g., ^{86}Sr).

Neodymium Isotopes

Nd isotopes, specifically the ratio $^{143}\text{Nd}/^{144}\text{Nd}$, are applied to both recent and ancient and carbonate and clastic sediments and sedimentary rocks. Neodymium isotope ratios in sedimentary rocks are commonly reported in epsilon notation ($\epsilon\text{Nd}(t)$), where the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is normalized against the chondritic uniform reservoir (CHUR) and both are corrected for radiogenic ingrowth of ^{143}Nd (DePaolo and Wasserburg 1976).

Neodymium isotope stratigraphy owes its utility to the fact that Sm is preferentially retained in mafic rocks relative to Nd, leading to a greater contribution of radiogenic ^{143}Nd resulting from decay of the parent isotope ^{147}Sm . This elemental fractionation gives rise to relatively radiogenic (higher $^{143}\text{Nd}/^{144}\text{Nd}$) mafic rocks and less radiogenic felsic rocks, which makes the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio a powerful tracer of sediment and solute sources. However, due to the low solubility of the rare

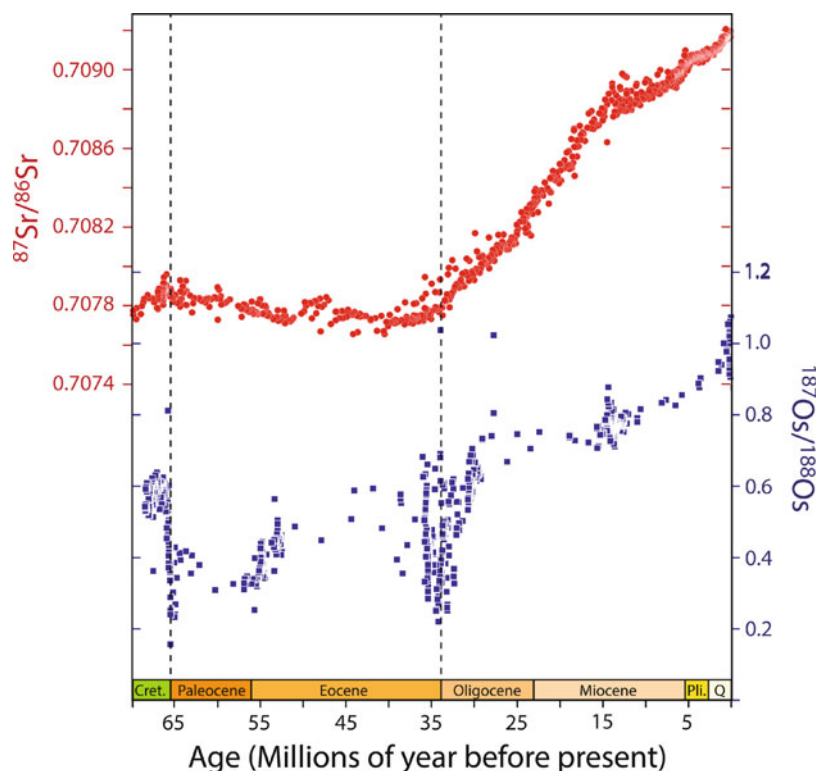


Fig. 8 Compilations of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{187}\text{Os}/^{188}\text{Os}$ data spanning from 70 million years ago until the present [Modified from Misra and Froehlich (2012)]. Note the short-lived anomalies in $^{187}\text{Os}/^{188}\text{Os}$ across the Cretaceous–Paleogene and Eocene–Oligocene boundaries (*dashed vertical lines*), which are not mirrored in the $^{87}\text{Sr}/^{86}\text{Sr}$ record.

earth elements (which include both Sm and Nd) in seawater, their tendency to adsorb to settling particles, and isotopic exchange between sediments and seawater, the effective isotopic residence time of Nd in the oceans is small: ~200–1,000 years (Tachikawa et al. 1999). Consequently, seawater is not uniform with respect to $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, and no unique seawater Nd curve can be generated. Rather, Nd isotopes, as typically measured in carbonates, phosphates, and ferromanganese nodules, are more commonly used to track the sources and circulation of ancient water masses (Banner 2004). Neodymium isotopes measured in fine-grained siliciclastic sediments are used to track tectonic, volcanic, and geographic evolution of the drainage basins supplying those sediments. To the extent that shifts in the initial $^{143}\text{Nd}/^{144}\text{Nd}$ composition of sediments can be linked to specific events, such as basement uplift or an episode of flood basalt magmatism, the Nd isotope record can have important chronostratigraphic applications to poorly dated sedimentary sequences.

Strontium Isotopes

Strontium isotope stratigraphy is one of the most powerful and widely applied chemostratigraphic tools to determine ages in otherwise undated marine rocks (see also entry on the ► [Seawater Sr Curve](#)). Similar to the Nd isotope system, strontium isotope ratios, namely, $^{87}\text{Sr}/^{86}\text{Sr}$, are useful because of the elemental fractionation between felsic and mafic rocks. In this case, Rb is concentrated in felsic rocks, resulting in higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in felsic continental crust from the decay of ^{87}Rb . In contrast, mafic continental and oceanic crust have low (unradiogenic) $^{87}\text{Sr}/^{86}\text{Sr}$. Distinct from Nd, however, the Sr budget of seawater includes not only a riverine input reflecting typically radiogenic continental sources but also a large unradiogenic component from the hydrothermal alteration of oceanic crust. The residence time of strontium is also much higher than neodymium:

4–5 million years, meaning that oceans are uniform with respect to $^{87}\text{Sr}/^{86}\text{Sr}$, except in rare cases where local water masses are heavily influenced by isotopically distinct freshwater or hydrothermal input.

Because the Sr^{2+} cation readily substitutes for Ca^{2+} , marine strontium isotope ratios can be preserved in evaporite, carbonate, and phosphate minerals precipitated directly from seawater. However, Sr isotope ratios are highly susceptible to diagenesis, during which these minerals are commonly subjected to loss of total Sr and input of radiogenic strontium from the detrital sediment fraction or meteoric fluids. Hence, constructing the seawater Sr curve (Fig. 7) and using Sr isotopes as a correlation and dating tools requires the selection of high-quality samples and a combination of petrographic and geochemical screening for the affects of diagenesis (McArthur et al. 2012).

The secular evolution of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 7) is conventionally interpreted in terms of competing influence of continental weathering (riverine) and seafloor hydrothermal Sr inputs. However, other factors also influence the long-term evolution of seawater Sr isotope ratios, including the progressive decay of ^{87}Rb , which imparts a long-term rise in $^{87}\text{Sr}/^{86}\text{Sr}$, and both tectonic (e.g., rifting or mountain building) and climatic effects. The result is a seawater Sr isotope curve with structure at multiple different timescales (Burke et al. 1982). Strontium isotope stratigraphy is most useful as a correlation and dating tool at time periods where $^{87}\text{Sr}/^{86}\text{Sr}$ changes rapidly (DePaolo and Ingram 1985), such as across the Permo-Triassic boundary and in the latter half of the Cenozoic (Figs. 7 and 8). Due to the considerable fluctuations in $^{87}\text{Sr}/^{86}\text{Sr}$ over the past billion years (McArthur et al. 2012; Fig. 7), obtaining a single, precise and accurate $^{87}\text{Sr}/^{86}\text{Sr}$ value from a marine sedimentary rock is not sufficient to establish a date. Rather, additional age or chemostratigraphic constraints, or a distinct $^{87}\text{Sr}/^{86}\text{Sr}$ profile is necessary to link to the composite strontium reference curve (Fig. 7). However, where this connection can be made, strontium isotope stratigraphy can be used in many cases to establish relatively precise (<1 m.y.) ages (McArthur et al. 2012).

Osmium Isotopes

Osmium isotope ratios, which owe their heterogeneity and utility to ongoing radioactive decay of ^{187}Re to ^{187}Os , are commonly reported as $^{187}\text{Os}/^{188}\text{Os}$ ratios. Osmium has a residence time in the modern oceans of 10–50 thousand years, and its isotopic composition ($^{187}\text{Os}/^{188}\text{Os} = 1.06 \pm 0.005$) reflects the balance between an unradiogenic mantle component ($^{187}\text{Os}/^{188}\text{Os} \approx 0.13$) and a radiogenic continental component ($^{187}\text{Os}/^{188}\text{Os} \approx 0.14$), with a small contribution from the dissolution of unradiogenic cosmic dust (Peuker-Ehrenbrink and Ravizza, 2000, 2012). Hydrogenous osmium is removed from seawater dominantly in metalliferous and organic-rich sediments. Whereas ferromanganese nodules serve as an important archive for Cenozoic Os isotope ratios (Fig. 8), organic-rich sediments are important in determining pre-Cenozoic $^{187}\text{Os}/^{188}\text{Os}$. However, because organic-rich sediments also concentrate Re, this requires an isochron approach to measure initial $^{187}\text{Os}/^{188}\text{Os}$ ratios.

As seen in Fig. 8, the Cenozoic marine Os isotope record ($^{187}\text{Os}/^{188}\text{Os}$) broadly resembles the Sr isotope record with both displaying a prominent, first-order rise toward more radiogenic ratios. However, due to the much shorter residence time of Os in seawater, it is sensitive to certain perturbations where the Sr isotope system is buffered. Specifically, prominent low $^{187}\text{Os}/^{188}\text{Os}$ excursion occurs across the Cretaceous–Paleogene and Eocene–Oligocene boundaries. The sensitivity of the Os isotope system to events such as flood basalt volcanism (Cohen and Coe 2002; Turgeon and Creaser 2008), abrupt warming (Ravizza et al. 2001; Schmitz et al. 2004), and large meteorite impacts (Paquay et al. 2008) highlights its importance as a chronostratigraphic tool. For example, Ravizza and Peuker-Ehrenbrink (2003) used Os isotope stratigraphy on deep-sea cores to

resolve the timing of Deccan Trap volcanism from the Cretaceous–Paleogene boundary and hence link the main mass extinction event to the Chicxulub bolide impact. Similarly, to the extent that events that were large enough to leave an imprint in the seawater Os isotope record are well dated, then the Os isotope system provides an indirect but robust way of dating sedimentary records.

Summary and Conclusions

Marine isotope stratigraphy is a widely applied tool in correlating and dating marine strata. It complements many other dating techniques, such as direct radiometric dating, biostratigraphy, and magnetostratigraphy. A large number of stable and radiogenic isotope systems are used in marine isotope stratigraphy, including both a core suite of well-established systems (C, O, and Sr) and a growing list of nontraditional isotope systems. Each isotope system has specific benefits and drawbacks, and no single system is universally applicable across sediment types and ages. Indeed, in many studies, multiple isotope proxies, along with other chemical stratigraphic tools, are applied, with each providing distinct constraints on the timing and origin of geological events. Important considerations in the application of isotope systems are the residence time and behavior of the chemical species of the element in seawater, the types of sediments in which the element is preferentially removed, and the potential of the isotope ratios to be preserved against diagenetic and metamorphic disturbances. Seawater isotope reference curves for the Cenozoic, and in some cases for the entire Phanerozoic, have been produced for many isotope systems, and these provide an excellent framework for indirect dating sediments and sedimentary rocks whose precise ages are not known.

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U-Th/He Dating

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Synonyms

(U-Th)/He dating; Helium dating; U-He dating; U-Th-Sm/He dating

Definition

U-Th/He dating is a method for determining the age of geological materials. The method is based on the accumulation of helium atoms produced by the alpha decay of U, Th, and in some cases Sm isotopes. Most recently, the method's chief use has been in measuring the temperature history of rocks at relatively low temperatures of between ~40 °C and ~250 °C.

Introduction

U-Th/He dating is the most venerable of all geochronological methods: the very first radiometric dates of any kind were helium dates reported at the very start of the twentieth century, starting with a 1905 lecture by Ernest Rutherford (1906; Strutt 1905, 1908). These early helium dates had perhaps the greatest intellectual impact of any ages ever measured. They provided independent and quantitative evidence for the great antiquity of rocks, thus establishing a modern framework for understanding Earth history and, of particular importance, providing firm evidence for the great spans of time required by biological evolution. Summaries of these heroic early measurements and their impact on the intellectual history of science can be found in a number of texts (e.g., Burchfield 1975; Hallam 1989; Dalrymple 1994; Lewis 2000).

History

For much of the twentieth century, work in geochronology focused on determining the absolute formation ages of rocks, and in this context the better results obtained by using the K-Ar, Rb-Sr, and U-Pb methods caused the development of U-Th/He dating to languish. From the 1950s to 1970s, studies of the mineral zircon and other materials such as corals, bone, and whole-rock volcanics continued intermittently but overall gave mixed results at best (Hurley 1954; Damon and Kulp 1957; Fanale and Kulp 1962; Fanale and Schaeffer 1965; Damon and Green 1963; Turekian et al. 1970; Bender 1973; Leventhal 1975; Ferreira et al. 1975).

Renewed interest in helium dating was rooted in the work of Dodson (1973), who provided a quantitative framework to explain how temperature-sensitive diffusion can result in “cooling” rather than formation ages for many minerals. Along with observations being made about the temperature significance of fission-track annealing (e.g., Wagner and Storzer 1972), this development launched the subdiscipline of thermochronology. Thermochronology turns the nuisance of

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apparently “reset” ages into a tremendous asset, given how important heat is in powering the solid Earth: fundamental geological processes such as magmatism, metamorphism, deformation, and erosion all significantly perturb local temperatures. Based on experience with fission-track and argon thermochronology, Zeitler et al. (1987) examined U-Th/He dating of apatite with the expectation that helium diffusion should be rapid at relatively low temperatures, and their measurements confirmed a closure temperature for helium retention during slow cooling of 100 °C or lower. At the same time, Lippolt and coworkers (e.g., Lippolt and Weigel 1988) began to explore helium dating of other phases.

In the early 1990s Ken Farley and colleagues wrote an important series of papers that confirmed and refined the results of Zeitler et al. (1987) on apatite, of greatest importance showing that the slow-cooling closure temperature of this mineral is close to 70 °C. These papers also developed basic analytical techniques and addressed the issue of helium loss by alpha ejection (e.g., Wolf et al. 1996; Farley et al. 1996). Subsequent to this essential work, the technique was extended to other minerals such as zircon (Reiners et al. 2002) and titanite (Reiners and Farley 1999), increasing numbers of laboratories were set up, and the technique became an important contributor to studies of landscape and basin evolution. To a significant degree, development of (U-Th)/He dating coevolved with a surge of interest in coupling between tectonic processes and surface processes, largely because the low temperatures that (U-Th)/He dating can address allow it to constrain the rates, timing, and magnitudes of erosion and incision.

Most recently, apatite (U-Th)/He geochronology was further extended by Shuster and Farley (2004), who developed the $^4\text{He}/^3\text{He}$ technique. By revealing diffusion gradients within individual grains of apatite, this approach can address temperatures as low as ~40 °C (Shuster et al. 2006). Current research in the field is addressing a better understanding of diffusion kinetics in minerals of interest, improved methods of coping with and even exploiting U and Th zoning, the use of laser spot analysis to improve sample throughput and accuracy as well as better handle alpha ejection, and the application of the method to a wider range of materials and problems in thermochronology and geochronology.

At this point the (U-Th)/He dating literature can appear dauntingly extensive. The review article by Farley (2002) provides a good comprehensive overview of the method. Many of the articles in the volume edited by Reiners and Ehlers (2005) comprise an excellent introduction to both technical issues and applications. The classic book by Ozima and Podosek (2002) and the volume edited by Porcelli et al. (2002) provide overviews of noble-gas geochemistry relevant to (U-Th)/He dating.

Systematics

Decay

Alpha particles associated with radioactive decay are ^4He nuclei and become neutralized to accumulate as atoms of ^4He , providing the basis for the U-Th/He dating method. A number of nuclides undergo decay by alpha ejection. Most of these are members of the decay chains associated with ^{238}U , ^{235}U , and ^{232}Th . Of the other naturally occurring nuclides that experience alpha decay, only ^{147}Sm may produce significant ^4He in some samples. The other nuclides have half-lives that are too long or abundances that are too small. Of the commonly dated materials, production from ^{147}Sm is usually important only in the mineral apatite.

The accumulation of ^4He in the U-Th-Sm/He system can be summarized as follows:

$${}^4\text{He} = 8 \cdot {}^{238}\text{U} \cdot (e^{\lambda_{238}t} - 1) + 7 \cdot {}^{235}\text{U} \cdot (e^{\lambda_{235}t} - 1) + 6 \cdot {}^{232}\text{Th} \cdot (e^{\lambda_{232}t} - 1) + 1 \cdot {}^{147}\text{Sm} \cdot (e^{\lambda_{147}t} - 1) \quad (1)$$

with decay constants $\lambda_{238} = 1.55125 \times 10^{-10} \text{year}^{-1}$, $\lambda_{235} = 9.8485 \times 10^{-10} \text{year}^{-1}$, $\lambda_{232} = 4.948 \times 10^{-11} \text{year}^{-1}$, and $\lambda_{147} = 6.539 \times 10^{-12} \text{year}^{-1}$; t is the elapsed time in years since the system closed, and ${}^4\text{He}$, ${}^{238}\text{U}$, ${}^{235}\text{U}$, ${}^{232}\text{Th}$, and ${}^{147}\text{Sm}$ are the amounts in moles. The decay constants for U and Th nuclides reflect the total decay to lead isotopes, and the pre-exponential coefficients in Eq. 1 account for the number of alpha decays produced in each decay chain. Note that compared to other dating systems, the (U-Th)/He dating enjoys a fast effective decay rate owing to the multiple alpha particles generated by each decay chain.

In most substances the modern production rate of ${}^4\text{He}$ is dominated by ${}^{238}\text{U}$ and ${}^{232}\text{Th}$; for equal amounts of *elemental* U, Th, and Sm, the relative production rates normalized to the production from Sm are

$${}^{238}\text{U} : {}^{232}\text{Th} : {}^{235}\text{U} : {}^{147}\text{Sm} = 1266 : 305 : 51 : 1 \quad (2)$$

keeping in mind that for modern U and Sm, ${}^{238}\text{U}/{}^{235}\text{U} = 137.88$ and ${}^{147}\text{Sm}$ is 14.99 % of total Sm.

Decay Chains and Secular Equilibrium. Equation 1 is only accurate for a system with decay chains that are in secular equilibrium, that is, a system in which the decay rate for all intermediate daughters is the same. This will be true for systems that have been in equilibrium for at least ~1 m.y., and thus for thermal history studies of preexisting rocks, disequilibrium will not be an issue. However, for applications that involve dating of young newly formed rocks like volcanics, the presence of disequilibrium must be assessed and if necessary corrected for (e.g., Farley et al. 2002). Note that disequilibrium can result in ages that are too old or too young, depending on whether during formation or alteration of the mineral phase or rock, longer-lived intermediate daughters like ${}^{230}\text{Th}$ have been lost or gained relative to equilibrium values.

Age Calculation

Equation 1 cannot be solved algebraically. An iterative technique such as the Newton-Raphson method can be used to obtain a solution to any degree of accuracy provided sufficient iterations are made (usually just a few are required). Meesters and Dunai (2005) derived a non-iterative approximation that uses a weighted mean decay constant having ${}^4\text{He}$ production rates as the weighting factors. Their expression is accurate to within 0.05 % for ages of less than 300 Ma and is quite useful for numerical modeling applications that involve very large numbers of age calculations. Vermeesch (2008) discussed alternative methods for calculating average ages when multiple aliquots of a sample have been analyzed, with the best data treatment depending on such factors as the number of grains analyzed per aliquot and the range in parent isotope composition.

Requirements and Assumptions for Age Determination

For a sample analysis to yield an age, (U-Th)/He dating shares a core set of requirements with other radiometric techniques. Above all, the sample in question must have been a closed system with respect to both parent and daughter nuclides, without changes due to processes such as weathering, alteration by fluids, or recrystallization. This requirement applies to attempts to determine the timing of either mineral formation or complete resetting, that is, it applies to geochronological applications. However, most (U-Th)/He dates that have recently been reported were measured for the purpose of thermochronology. In this context, the core requirement is that the sample in question has been

closed with respect to parent nuclides and that the observed daughter product represents the net result of accumulation due to radioactive decay and loss due to thermally activated diffusion.

Note that unlike other methods of noble-gas dating like the K-Ar method, (U-Th)/He ages are calculated without any correction for atmospheric contamination. Given the very large $^4\text{He}/^3\text{He}$ ratio in the atmosphere ($\sim 730,000$) and the great variability of this ratio in geological environments, applying a correction would be difficult; this difficulty is compounded by the exacting technical requirements for measuring very small amounts of ^3He at natural abundance levels. Fortunately, the concentration of ^4He in the atmosphere is low (5.2 ppm), and any adsorbed atmospheric ^4He will be rapidly removed under vacuum conditions prior to analysis (Ozima and Podosek 2002). The bottom line is that experience with dating age standards has shown that a correction for atmospheric ^4He is not required.

Accuracy and Precision

The component methods routinely used in conventional (U-Th)/He dating can achieve analytical precisions of 1–2 % depending on sample size, age, and U and Th concentration. Most laboratories monitor their work using internal standards as well as widely used de facto standards such as Durango apatite (31.4 Ma; McDowell et al. 2005) and Fish Canyon zircon (28.48 Ma; Schmitz and Bowring 2001). Replicate analyses of standards and calibration gases verify the accuracy of the method and its precision with respect to laboratory methods. Analyses of some unknowns, in particular slowly cooled samples, often show greater scatter, with precision on replicates at times approaching 10 % at the 95 % confidence level. This is not surprising given the range of factors that can influence the diffusive properties of a single grain (see below) – under conditions of slow cooling, even small difference in diffusivity can translate into large differences in measured age.

Alpha Ejection

Alpha decay involves ejection of an energetic ^4He nucleus from its parent nuclide, with energies in the range 4–8 MeV, and Farley et al. (1996) first addressed the implications of this ejection for (U-Th)/He dating. The distance traveled by the alpha particle, termed its stopping distance, will vary depending on its kinetic energy and the nature of the medium through which it is traveling. For typically analyzed minerals (apatite, zircon, and titanite), these stopping distances range from roughly 15–25 μm for various members of the U and Th decay chains (Ketcham et al. 2011). Due to the minimum amounts of sample mass needed for U, Th, and He analyses as well as the natural size distributions of accessory minerals in many rocks, grains of 50–100 μm in radius are usually analyzed. As a result, alpha ejection will clearly impact the helium content of such grains: for example, a spherical grain of apatite 50 μm in radius would suffer some 25 % of helium loss due to ejection.

It is possible to calculate a correction factor F_t to account for ejected helium. F_t gives the fraction of alpha particles lost to ejection and depends on grain size and shape. Spherical grains can be treated with a simple analytical expression. Other geometries require Monte Carlo simulations to determine geometry-specific coefficients that can be used to calculate F_t based on the grain's surface-to-volume ratio. Ketcham et al. (2011) provided a detailed investigation and updated tabulation of correction factors and protocols. Complex 3D geometries in general require direct Monte Carlo simulation of the exact grain shape. Very large samples or internal samples for which all material is in effect more than one stopping distance from the surface obviously do not require an alpha-ejection correction to be made.

Once an F_t correction factor has been calculated that reflects the content-weighted contributions from U, Th, and Sm, the measured age is adjusted to account for missing alphas by correcting the sample's helium concentration and then recalculating the age:

$${}^4\text{He}_{\text{corrected}} = {}^4\text{He}_{\text{measured}} / F_t \quad (3)$$

For young ages of $< \sim 100$ Ma, it suffices within 0.1 % to apply the correction to the age itself; beyond that the nonlinearity in helium accumulation over time requires the correction to be made on the helium content, not the age. Note that this correction can also be viewed as an adjustment to the efficiency of U and Th decay in producing alpha particles that are retained.

This correction is accurate for quickly cooled samples that are deficient in helium due to alpha ejection. For samples with complex thermal histories in which the helium content represents a balance between loss by diffusion and accumulation by decay, alpha ejection will modify the diffusion profile. Accurate modeling requires mathematical treatment of the complete diffusion/ejection/accumulation process and interpretation of the resulting ages in this context. However, for samples having simple monotonic cooling histories, Eq. 3 gives appropriate results that restore ages to values consistent with the sample's cooling history.

Diffusion

From the very beginning of geochronology, workers were aware that (U-Th)/He ages will likely be minimum ages, owing to the ease with which the small helium atom can diffuse through materials (e.g., Rutherford 1906; Strutt 1909). As noted above, this mobility explains both the relatively infrequent use of the method for much of the twentieth century and the great expansion in its application over the past 20 years. Helium is a highly incompatible trace element in minerals, so to first order, helium diffusion occurs according to the well-understood principles of simple volume diffusion. While relatively little quantitative is known about He solubility in rocks and minerals, especially at high temperatures and pressures (see Ozima and Podosek 2002 for a discussion), it is known that helium solubility in geological materials is extremely low. Common laboratory experience with noble gases shows that they will diffuse out of minerals when heated, even in the presence of significant He and Ar (e.g., if heated when exposed to atmosphere). Experimental evidence suggests that for apatite, the most commonly dated mineral, the physical grain itself is the effective diffusion dimension, not some interior domain (Farley 2000). As such, it is relatively simple to perform diffusion experiments using the assumption that the concentration at the crystal margin is zero and so determine diffusion data at various temperatures. Such kinetic data enable the application of U-Th/He dating to thermochronology and also permit assessment of whether a particular (U-Th)/He determination is likely to represent an original age or be an overprinted or a cooling age. Harrison and Zeitler (2005) provide an overview of the fundamentals of noble-gas thermochronometry.

Radiation Damage

Sufficiently large combinations of either time or U and Th concentration can lead to accumulated alpha-radiation doses that are sufficient to break down crystal structures, a process known as metamictization. This will significantly alter diffusion properties and the retentivity of minerals. Fortunately, the effect is not observed in lower-U minerals like apatite and titanite and is modest even in higher-U phases like zircons. Reiners (2005) notes that to influence the diffusion properties and retentivity of zircons, radiation doses equivalent to several hundred millions of years of accumulation in a 1,000 ppm grain are required. For monazite, Boyce et al. (2005) noted that

closure to helium diffusion takes places at substantially higher temperatures than annealing of radiation damage, such that the kinetics of closure will not be impacted by radiation damage; in addition, the relatively low temperature for radiation damage annealing in monazite suggests that low-temperature post-closure leakage of helium should not be common.

In apatite, Shuster et al. (2006) and Flowers et al. (2009) have shown that accumulation of radiation damage in the modest amounts typical for this mineral leads to a counterintuitive increase in retentivity, rather than any leakage. The likely explanation for this behavior is that radiation damage serves as isolated traps for diffusing helium atoms, retarding the progress of their normal diffusion jumps. The effect appears to be quite reproducible and is a function of U and Th content, time, and also thermal history because at higher temperatures the radiation damage will anneal away. Although this makes calculations more complex, the effect may actually be useful by creating a spread in retentivities within a single apatite population proportional to its variation in U and Th content (Flowers 2009; McKeon et al. 2014).

Artifacts and Other Issues

Several technical and sample-specific issues complicate (U-Th)/He dating and need to be considered when assessing dating results. Fitzgerald et al. (2006) discussed a number of these.

Unlike the case of K-Ar dating, where potassium is a major element in the host mineral or rock, the parent nuclides for (U-Th)/He dating tend to be trace or minor elements that can be distributed with considerable zoning; U and Th variations of 10× or far more are possible and commonly observed in zircon and, to a lesser degree, apatite. The greatest problem associated with such zoning is that it confounds a simple alpha-loss correction that is based on a bulk estimate for a grain's He content and the assumption that U and Th are uniformly distributed. In the end-member case where all parent nuclides are more than one stopping distance from the surface, no F_t correction would be needed, and applying one would lead to an age overestimate of some 10–20 % or more. The other extreme, where all parent nuclides are located only across a grain's surface, would lead to an underestimate of the amount of alpha ejection and could in theory lead to a 50 % or greater underestimate in age. In practice, zoning can be assessed using sample characterization (microprobe analyses, radiographic imaging) and to some degree by analysis of replicates (which will be misleading if mineral grains are all consistently zoned). It is worth noting that the end-member scenarios are unlikely, and the reasonable mean ages seen in many samples along with only a slightly greater-than-expected scatter between aliquots are probably evidence for only mild zoning in most samples. In the special case of helium implantation from a grain's surface or external sources, Spiegel et al. (2009) showed that abrasion of grain exteriors can greatly improve both accuracy and precision for ages, but this approach is of no significant help for zoning interior to a grain because in a zoned grain, ejection of helium between zones will occur and it is impossible to know if any abraded material was either a sink or source for helium. Methods of better handling zoning remain an area of particularly active research and technique development.

Mineral inclusions can serve as sources of unexpected “extra” ^4He , and if the method chosen to measure U and Th does not equally sample the inclusions as well as the bulk grains, this extra He will be “parentless” in terms of the age analysis. This is of greatest concern if there are refractory inclusions of a high-U or high-Th phase in an easily dissolved, lower-U phase like apatite. The problem can be minimized by careful grain selection; just as with other dating methods, good data simply require good samples and care in their selection and preparation. Alternatively, samples can be dissolved using methods that guarantee total dissolution, in which case any small inclusion ends up behaving as point source of helium. This can improve replication between aliquots (Vermeesch et al. 2007).

Grain size and variations in grain integrity can also lead to age scatter and imprecision if not addressed, especially from very slowly cooled rocks where subtle variations can amplify difference in age. As predicted from diffusion theory, grain size controls retentivity, as demonstrated empirically by Reiners and Farley (2001), so it is important to keep grain sizes similar, certainly within an aliquot. Brown et al. (2013) pointed out that analysis of broken crystals that expose internal volumes can lead to significant age dispersion in slowly cooled samples. Because apatite has a strong parting perpendicular to its C-axes, it can be difficult to identify broken grains even for well-crystallized euhedral prisms. Both grain size and fragment effects can be used to recover thermal history information, but this requires good sample characterization and experimental planning.

Analytical Methods

Materials

Most modern U-Th/He dating has been done on the minerals apatite (Zeitler et al. 1987; Farley 2000), zircon (Reiners et al. 2002), titanite (also called sphene; Reiners and Farley 1999; Stockli and Farley 2002), and monazite (Boyce et al. 2005). Interesting data have also been obtained for epidote and garnet (Nicolescu and Reiners 2005), hematite (Lippolt et al. 1993), magnetite (Blackburn et al. 2007), complex substances such as weathering rinds and oxides (Lippolt et al. 1998; Shuster et al. 2005), and even gold (Cabral et al. 2013). For most laboratories, only single crystals need to be analyzed except for very young samples. However, for conventional work it is important to choose unbroken crystals of similar shape and size, free of mineral and fluid inclusions, so in practice it is important to obtain several hundred crystals from which to select samples. Although there is great variation between rock types and sample to sample, mineral-separation processing of 0.5–1 kg of material is necessary for routine work.

The accessory minerals most often used in U-Th/He dating are quite common in a wide variety of rock types. Zircon in particular occurs very frequently, albeit in small amounts. For analyses aimed at determining the formation age of a rock, felsic volcanic rocks are the most useful as they cool nearly instantly and frequently contain zircon and other accessory minerals. Studies of thermal history require rocks that formed or have been reheated at sufficiently high temperatures to “zero” the (U-Th)/He clock. Conversely, provenance studies that use U-He ages as tracers require clastic sedimentary rocks that have not been buried and reheated to temperatures that have perturbed the helium concentration of the mineral(s) of interest.

Conventional Analyses

Conventional U-He work involves extraction and measurement of ^4He from a sample using a noble-gas mass spectrometer connected to an ultrahigh vacuum system, followed by the measurement of U, Th, and if appropriate Sm content using isotope-dilution analysis by ICP/MS. Measurement of ^4He is possible in a relatively inexpensive quadrupole mass spectrometer, although a full magnetic-sector instrument can also be used. Helium is liberated from samples by heating, either in a vacuum furnace or by laser. The gas-extraction line must be connected entirely of metal owing to the high diffusivity of helium in glass.

Typical Conventional Analysis. After selection of grains for analysis, they are photographed to record their shape and dimensions (necessary for calculation of the alpha-ejection correction). Note that unlike the traditional K-Ar method, where different splits of samples are used for potassium and argon analysis, for (U-Th)/He dating it is essential to make all measurements on the same sample given the variability in U and Th between grains. The selected grains are loaded in small niobium or

platinum packet, loaded into the vacuum system, and, after baking to achieve a clean vacuum, heated by either a resistance furnace or a laser. The evolved gas is purified of active gases, and its helium content is then measured, usually by spiking, that is, by adding a pipetted ^3He aliquot of known amount. Performance of the mass spectrometer in measuring ratios is monitored using a pipette of known $^4\text{He}/^3\text{He}$ ratio and ^4He amount, and age standards are run along with unknowns to monitor overall performance of the system over the longer term.

Once samples have been outgassed, they are retrieved from the vacuum system and subjected to U-Th-Sm analysis. This involves acid digestion appropriate to the mineral or material in question and spiking with U and Th isotope tracers. These solutions are then analyzed using ICP/MS methods to determine U, Th, and Sm if likely to be present, e.g., in apatite.

To get a sense for what these analyses entail, a grain of the Durango apatite standard will contain about 3.5×10^{-13} mol of ^4He , 1.5×10^{-12} mol of ^{238}U , 3.0×10^{-11} mol of ^{232}Th , and 5×10^{-12} mol of ^{147}Sm . The time for analysis of a batch of say 10 samples, including mineral separation, sample picking and loading, He analysis, and U-Th-Sm analysis, would take perhaps 5–10 working days.

Laser Spot Analyses. Several laboratories are actively pursuing direct laser-ablation analysis for both He as well U and Th. High-power excimer laser systems have been developed that cleanly excavate pits of regular geometry within single grains without heating. Such systems require sequential analysis, first for helium and then again for U and Th. Challenges to the method are the need to obtain sufficient helium for an acceptable analysis and in calibrating the He and U-Th concentrations with respect to one another. Boyce et al. (2006) have reported encouraging data from monazite. Although the equipment needed is more elaborate than for conventional analysis (it costs more to dig a smaller hole!), potential advantages of this approach are higher sample throughput, better handling of U-Th zoning, and avoidance of the need to make an alpha-loss correction since the edges of a grain can be avoided. Drawbacks include the higher equipment cost, the challenge of analyzing single grains of younger, lower-U apatites, and difficulties in accurately recording any fine-scale diffusion profiles near grain edges.

$^4\text{He}/^3\text{He}$. This variant of the (U-Th)/He method was developed by Shuster et al. (2004) and Shuster and Farley (2004). The technique involves proton irradiation to convert a range of atoms in the target mineral to ^3He nuclei; because most atoms in the mineral serve as targets, the ^3He will be uniformly distributed. By analogy to the $^{40}\text{Ar}/^{39}\text{Ar}$ method, this ^3He provides a reference by which the distribution of ^4He can be inferred through stepwise heating. However, because the ^3He is not produced from the parent nuclides U and Th, the $^4\text{He}/^3\text{He}$ ratio of a heating step cannot determine a geological age in the way that a $^{40}\text{Ar}/^{39}\text{Ar}$ ratio can; determination of age spectra require calibration of the bulk $^4\text{He}/^3\text{He}$ ratio against the conventionally determined bulk age of the sample. The method requires use of a sensitive noble-gas sector mass spectrometer due to the small amounts of ^3He produced by proton irradiation as well as the need to resolve this ^3He from isobaric interferences such as HD. The method also requires pristine apatite grains of regular geometry that are not zoned in U and Th.

A great advantage of the technique is that it permits recovery of a continuous segment of an apatite sample's thermal history and can also determine an individual sample's kinetics as part of the step-heating experiment. This allows apatite $^4\text{He}/^3\text{He}$ dating to address a temperature range of ~50 °C beginning at temperatures as low as 40 °C, greatly extending applications of (U-Th)/He thermochronometry to crustal levels as shallow as 1–2 km.

Applications

(U-Th)/He dating has been applied to a great range of problems in the Earth sciences. Most of these applications have revolved around the temperature sensitivity of the technique and the way that various geological processes alter temperature in the Earth. Full appreciation of the impact of (U-Th)/He dating requires some understanding of the principles of thermochronology as well as an appreciation for how particular sets of processes can lead to setting or resetting of the (U-Th)/He system. The following set of studies illustrate the great range of applications of the (U-Th)/He method.

Tectonics and Erosion

Erosion will alter the temperature field beneath the surface, and in many environments such as mountain belts, erosion occurs in response to uplift of this surface; the two processes can in some circumstances become coupled due to isostasy and crustal dynamics. A number of studies have used (U-Th)/He dating to examine the timing of rock uplift, erosion, and the interplay between the two in mountain belts, across a great range of time scales. For example, Finnegan et al. (2008) examined feedbacks between tectonics and erosion in the extremely active northeastern Himalaya, where (U-Th)/He cooling ages can be as young as 0.4 Ma. In contrast, Flowers et al. (2006) examined rocks in the Canadian Shield that give exceptionally old apatite (U-Th)/He ages of up to ~1,000 Ma, thus documenting equally exceptional crustal stability over this time period. When combined with fully 3D thermomechanical models, (U-Th)/He and other thermochronological data of sufficient density can be inverted for comprehensive constraints on the timing or rates of deformation and erosion, as shown by van der Beek et al. (2010) for the morphological evolution of the Western Alps.

Landscape Evolution

The (U-Th)/He technique has permitted geologists to go beyond broader estimates of orogenic evolution to focus on such specific processes and features as relief development and incision. House et al. (1997, 1998) used the (U-Th)/He method to date the topographic evolution of the Sierra Nevada and show that relief in these mountains is old. Shuster et al. (2011) used $^4\text{He}/^3\text{He}$ data to determine the timing and pervasive nature of fjord cutting in southern New Zealand, and Flowers and Farley (2012) used apatite (U-Th)/He and $^4\text{He}/^3\text{He}$ data to make the controversial argument that parts of the Grand Canyon are quite old. Workers are also beginning to apply (U-Th)/He dating to suites of detrital minerals found in sandstones, as these minerals give a unique form of thermochronological provenance information, particularly if multiple methods are applied to each grain (double or even triple dating; e.g., Rahl et al. 2003).

On a shorter time scale and at locations nearer to or at the Earth's surface, clever applications of (U-Th)/He methods can return valuable information about the nature of processes. Riihimäki et al. (2009) used the thermal overprint associated with the formation of clinkers, produced by spontaneous combustion of coal, to determine the rate and timing of arroyo cutting, linking this to climate fluctuations. Reiners et al. (2007) examined apatites from hillslopes and stream channels in an attempt to constrain wildfire impact and frequency.

Geochronology and Stratigraphy

Although far less common in the “modern” era of (U-Th)/He dating, the method has been used in a strictly geochronological context and this will continue. Farley et al. (2002) examined the dating of tephra using zircon and apatite, and Blondes et al. (2007) dated young basalt lavas using entrained xenocrystic zircons. Shuster et al. (2005) investigated the use of weathering products to date laterite

formation. Finally, successful work on magnetite (Blackburn et al. 2007) and gold (Cabral et al. 2013) opens up the possibility of using the (U-Th)/He method to date ore deposits.

Conclusion

With numerous laboratories now in operation and nearly 2,000 journal articles published, (U-Th)/He dating is clearly a mainstream tool for earth scientists interested in the timing and rates of a number of surface and near-surface processes. Given research currently in progress, improvements in accuracy and precision are likely to be forthcoming due to an increased understanding of both the kinetic behavior of helium loss as well as technical artifacts such as U and Th zoning. Technical advances such as laser-probe dating should contribute to this, and by improving sample throughput, these advances should increase the volume of data that can feasibly be brought to bear on a research question. Laboratory advances in sample handling and measurement also hold promise of dating new materials in such challenging locations as the very near-surface and diagenetic environments.

Acknowledgment

Thanks to Ken Farley for the useful comments that helped me clarify several technical points.

Cross-References

- ▶ [Apatite](#)
- ▶ [Fission Track Dating](#)
- ▶ [Geochronology](#)
- ▶ [Historical Development \(of Dating Methods\)](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Noble Gas Mass Spectrometer](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Zircon](#)

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Geomagnetism

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Synonyms

[Earth's magnetic field](#)

Definition

Geomagnetism is a domain of geophysics which studies the origin and nature of the Earth's magnetic field. Geomagnetism involves integrated approaches to decipher ancient and contemporary magnetic fields of the Earth and other planets of the solar system.

Structure and Properties of the Earth's Magnetic Field

The Earth's magnetic field or geomagnetic field surrounds the planet where $\sim 98\%$ of it the field generated by geodynamo, creating the magnetosphere (Merrill et al. 1996). Geodynamo is the compositional and thermal convection in the outer liquid core of the conductive material (mainly iron). Convective electrical current produces geomagnetic field. The main part of the field is produced in the Earth's core and is described near the Earth's surface as a magnetic field of a dipole (Jones 1977; McFadden and Merrill 1984). The dipole has its magnetic South Pole oriented toward the geographical North Pole (see Fig. 1). The field structure is deformed by the solar wind above the Earth's atmosphere (1–2 % of a total measured field at the Earth surface) (Courillot and Le Mouel 1988). In reality, there is a deviation between the best-fit dipolar magnetic field on the Earth and the actual field. In the mantle, the shape of the magnetic field is changed to a quadrupole or multipole system. Additional disruption of the field (1–2 %) comes from the magnetized crustal rocks (Merrill 2010).

Presently, the horizontal component of the field is directed roughly into the geographic north–south direction. The local deviation from this alignment is called declination (see Fig. 2). In the middle and high latitudes, the magnetic flux lines change from the pointing horizontally vector to a much stronger more vertical vector (see Fig. 1). The inclination angle of the field lines can be measured with a compass needle, whose axis of rotation is mounted horizontally (see Fig. 2). At the magnetic North and South Poles, the inclination is 90° , and at the magnetic equator, it is 0° . Currently, the axis of the geomagnetic dipole field deviates at about 11.5° relative to the Earth's axis of rotation. The present-day dipole moment of the geomagnetic field is $M = 7.746 \times 10^{22} \text{ Am}^2$ and can be calculated from the most recent International Geomagnetic Reference Field of 2010 (IGRF-11) (International Association of Geomagnetism and Aeronomy, Working Group V-MOD 2010). It changes constantly with the current annual decrease of $-0.006 \times 10^{22} \text{ Am}^2/\text{year}$.

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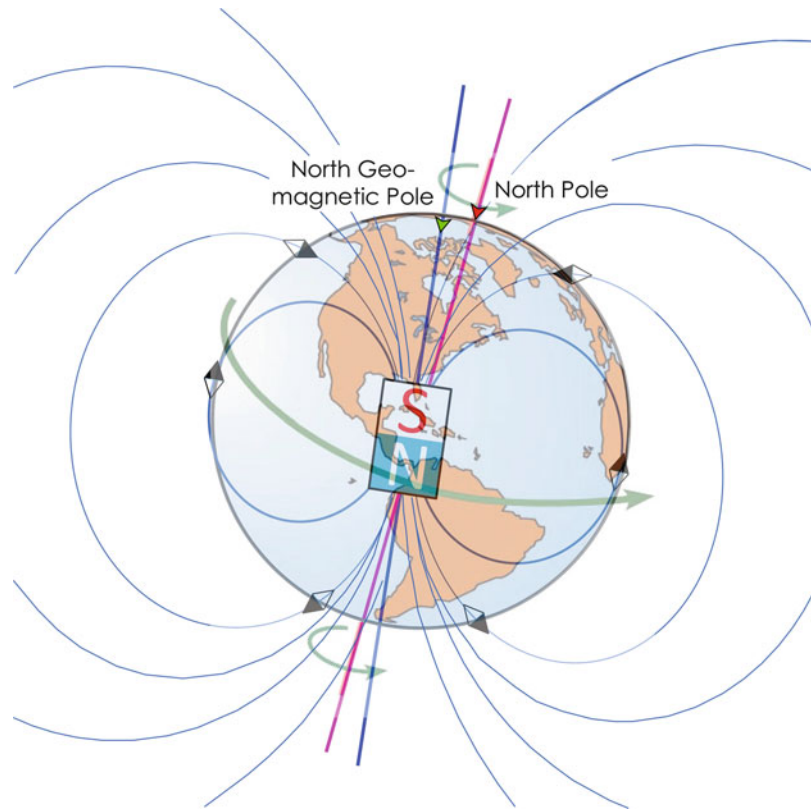


Fig. 1 The geomagnetic dipole position in the center of the Earth with its axis tilted relative to the Earth's axis. Magnetic field lines are shown with horizontal magnetic compass needle pointing along the lines. The needle indicates magnetic inclination, the angle measured from the horizontal surface at the point of observation. Positive values of inclination indicate that the magnetic field of the Earth is pointing downward, into the Earth, and negative values indicate that it is pointing upward

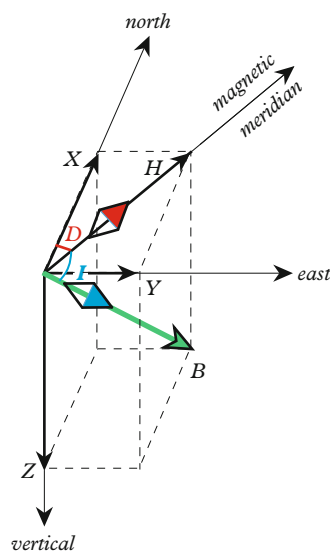


Fig. 2 Illustration of the coordinate systems used for representing the Earth's magnetic field. The geomagnetic field can be described by north (X), east (Y), and vertically downward (Z) Cartesian components and by the angles of declination (D) and inclination (I) together with the total field intensity (B)

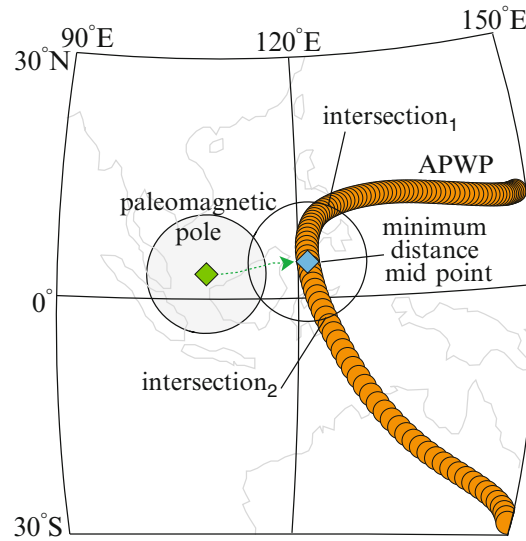


Fig. 3 Illustration of the paleomagnetic age determination (modified from Blanco et al. (2013) with Elsevier permission). The pole and the circle of confidence are projected over the minimum distance point on the APWP. The intersection points 1 and 2 will constrain the error in age

Paleomagnetism

Paleomagnetism studies the past geomagnetic field recorded in rocks and sediments. Since the magnetic minerals are abundant in the Earth's crust, paleomagnetic studies can be applied to a wide range of rocks and sediments. When a rock, containing ferromagnetic minerals, is heated to temperatures above the Curie point and then cooled in the ambient geomagnetic field, it is magnetized in the direction of the existing geomagnetic field (McElhinny and McFadden 1999; Tauxe 2010). This applies to volcanic rocks, bricks, pottery, and terracotta. During sediment formation, the magnetic grains align themselves with the local magnetic field until they become locked into place. The acquired magnetization is called a remnant magnetization and can be described by its inclination, declination, and intensity or by the related values of paleolatitude and paleolongitude which define a virtual geomagnetic pole (VGP). When a sequence of VGPs (paleomagnetic poles) has reliable ages, they can be used to produce an apparent polar wander path (APWP). This path is constructed using different poles of known age for a stable continental block and represents the APWP through time for that continent (Tauxe 2010).

Geomagnetic Reversals, Excursions, and Secular Variations

The direction of the ancient magnetic field has been continuously registered in the mid-ocean ridges when the erupted magma cools down. It enables one to study the geomagnetic polarity reversals, i.e., when the Earth dipolar field reverses 180° relatively to the present-day orientation. Such reversals are common throughout Earth's entire geological history. The most recent polarity reversal occurred at ~780,000 years ago (Brunhes-Matuyama reversal) (Langereis et al. 2010). Recent study suggests that an actual pole shift takes around 1,000 years (Valet et al. 2012). Reversals are very well documented until about 160 million years ago from the marine magnetic anomalies (Cande and Kent 1995; Gee and Kent 2007) and are less reliably known for older geological times.

A geomagnetic excursion is a significant change in the prevailing geometry of the geomagnetic field, which lasts on the order of the first thousands of years. The geomagnetic field, however, does not flip to a stable position at 180° during excursion. The most common contemporary conception states that the excursion occurs due to localized disturbances in the geomagnetic field caused by the convection of electrical currents in the outer core and its interaction with the mantle (Olson et al. 2013).

Geomagnetic secular variations are the changes in the field over periods of a year or more; they reflect shorter-term changes in the Earth's outer core. The variations that predate historical observations and recorded in archaeological and geological materials are called paleomagnetic secular variations or paleosecular variations (PSV).

Paleomagnetic Dating

For paleomagnetic dating, the APWP is used to determine the age of a paleomagnetic pole obtained from rocks or sediments of undefined age by projecting the pole on a sphere to the nearest point on the APWP (Symons and Sangster 1991; Blanco et al. 2013) (see Fig. 3).

A similar idea arises with PSV. The secular variation reference curves are created to display inclination, declination, and the intensity of the magnetic field for a given region through time. The PSV curves are typically defined for only the last few thousand years, which is useful when dating young material such as archaeological artifacts (Hangstrum and Blinman 2010; Pavon-Carrasco et al. 2011; Tanguy et al. 2003). Recently there have been great strides made in creating well-defined techniques and useful computer software to date archaeological artifacts using inclination, declinations, and intensities (Le Goff et al. 2002; Pavon-Carrasco et al. 2011).

Magnetostratigraphy

Polarity change is a global phenomenon which occurs simultaneously all over the world. Magnetostratigraphy studies polarity change registered in the geological sections, drilling cores, and magnetic anomalies in the ocean. The polarity change pattern can be used for stratigraphic correlation and dating of the geological section separated from meters to thousands of kilometers. Creating a universal reference scale of polarity changes using biostratigraphic and radiometric ages produces the geomagnetic polarity time scale (GPTS). This scale provides valuable stratigraphic markers for short- and long-range correlations of geological sections (Langereis et al. 2010). Oceanic and marine magnetic anomalies are very important for determining the spreading velocities between two plates on either side of a mid-ocean ridge.

Paleointensity

The value of ancient intensity of the geomagnetic field is called geomagnetic paleointensity. Independent records of paleointensity from sediment cores in different areas of the world are stacked together and represent the reference curve of the variations of the geomagnetic dipole moment (Valet et al. 2005; Channell et al. 2009). This provides information regarding the processes governing the geodynamo. So far, this procedure has been limited to the last two million years. The reference curve from the sedimentary records is calibrated with the absolute dipole moments derived from volcanic

lavas. Intervals of low intensity often correspond to the geomagnetic excursions and reversals. Comparison of the continued paleointensity records for sediments with unknown age to the reference paleointensity curve results in a possibility to date sediments when other means of dating are not reliable (e.g., Lake Baikal sedimentary cores, Kravchinsky et al. [2007](#)).

Archeomagnetism

Archeomagnetism is based on the variation of the intensity and direction of the geomagnetic field, and on the property of baked clay to record the situation during firing, as it remains fixed in the arrangement of the particles of iron oxides in it, immobilized by heating temperatures of about 650–700°.

The direction of the Earth's magnetic field does not vary in a consistent manner over time or space, and the changes have been recorded by scientists from only the sixteenth century. It is therefore necessary for each region to determine what were the geomagnetic changes through the examination of samples which remained in the same position from the time of heating. In the field of archaeology, once the reference curves are established, this can be used for dating other artifacts (Tarling [1975](#)). The accuracy of dating can vary depending on the rapidity of changes in the Earth's magnetic field at different times, and in general, it is possible to obtain ages with accuracy of decades or quarter century. While other forms of dating are based at the decay of radioactive elements, such as carbon dating, magnetic dating allows archaeologists to figure out the age of more varied and older artifacts.

Summary

The main geomagnetic field is formed in the outer core of the Earth and can be measured on the surface or in space. In the first approximation, the geomagnetic field of the Earth can be represented by the field of a dipolar magnet placed in the center of the planet. Geomagnetic poles migrate at the Earth's surface continuously, and reversals of the geomagnetic field direction occurred many times in the Earth's geological history. Short-term and long-term changes of the geomagnetic field are constantly monitored and studied by geophysicists because they carry important information about the current state of the geomagnetic field and past magnetic events.

The magnetic field has an effect on a variety of phenomena on Earth, in the atmosphere, and closest space. Magnetic measurements are commonly used for chronology and are important in geophysical exploration, for navigation, aerospace, and geodesy.

Cross-References

- ▶ [Archeomagnetic Dating](#)
- ▶ [Geochronology](#)
- ▶ [Geological Time Scale](#)
- ▶ [Magnetic Anomalies](#)
- ▶ [Magnetic Chronology](#)
- ▶ [Magnetism, Rock and Mineral](#)
- ▶ [Magnetostratigraphic Dating](#)
- ▶ [Paleomagnetism, Marine Sediments](#)

- [Paleomagnetism, Terrestrial Sediments](#)
- [Potassium Argon, Volcanic Rocks](#)

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Impact Glass (Fission Tracks)

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Definition

Glass formed by melting of a siliceous rock exposed on the Earth surface due to the impact of a meteorite with the ground. Fission-track dating is a radiometric dating technique used for dating those glasses, and it is based on the damages (tracks) produced by the decay by fission of ^{238}U .

Introduction

Innumerable extraterrestrial bodies reach our planet every day. Most of them, due to their high speed, fully vaporize when they cross the atmosphere or their size is strongly reduced. So, these meteorites do not produce relevant effects. Only the largest bodies have probability to reach the Earth surface with a kinetic energy sufficient to produce recognizable impact structures. Luckily, large-sized meteorites are rare in comparison with the high number of those that reach the terrestrial atmosphere. For this reason impact craters, which are evidence of a collision of a heavy body occurred sometime in the past, are relatively rare. The fall of a large meteorite may have catastrophic effects, such as long-lasting climate changes. It is known that the abrupt ecosystem changes with extinction of many species, which represent the Cretaceous/Tertiary boundary, might be correlated to such an event. Therefore, it is an important task to study the chronology of significant impacts in order to establish possible correlation with environmental changes and to investigate on their periodicity, if any.

During an impact, due to transferring of a high amount of kinetic energy to the ground, target rocks suffer high shock-wave pressures, and their temperatures grow instantaneously up to 1,000 °C. This phenomenon, named shock-wave metamorphism, involves various effects – such as vaporization, melting, and fracturing – depending on the kinetic energy of the extraterrestrial body and on the original setting of the rock in relation to the impact. When duration and amount of temperature are sufficient to provoke the total annealing of preexisting tracks in a mineral phase containing U as trace element, the fission tracks one can etch and count are those formed after the impact, and the resulting age is the age of the impact itself. Thus, the fission-track technique may result to an efficient method for the age determination of impacts, providing that a suitable mineral phase is present in the target rocks. For the lower thermal stability of fission tracks and for its abundance, apatite is commonly preferred, but also sphene and zircon have been used. A crucial point is to establish whether the total annealing of preexisting tracks really occurred. Therefore, track length measurements are needed in order to compare their distribution with those of rocks that suffered fast cooling, such as volcanic rocks.

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Table 1 Impact structures dated using the fission-track method since the fission tracks early times (Modified after Wagner and Van den Haute (1992))

Structure	Material	Age (Ma)	Correction techn.	Reference
1. Henbury	Glass	0.0042 ± 0.0019		Storzer and Wagner (1977)
2. Wabar	Glass	0.0064 ± 0.0026		Storzer (1971)
		0.0064 ± 0.0025		Storzer and Wagner (1977)
3. Köfels	Glass	0.008 ± 0.006		Storzer et al. (1971)
		0.0089 ± 0.0029		Storzer and Wagner (1977)
4. Darwin	Glass	0.37 ± 0.76		Fleischer et al. (1969a)
		0.72 ± 0.04		Gentner et al. (1969)
		0.71 ± 0.01		Gentner et al. (1973)
		0.74 ± 0.04	Size	Storzer and Wagner (1977)
5. Bosumtwi	Glass	1.04 ± 0.20		Gentner et al. (1967)
		$0.32 \pm 0.19, 1.48 \pm 0.47$		Fleischer et al. (1965)
				Fleischer and Price (1967)
		1.03 ± 0.02		Storzer (1971)
		1.04 ± 0.11	Size	Storzer and Wagner (1977)
6. Zhamanshin	Glass	1.07 ± 0.05	Plateau	Storzer and Wagner (1977)
		1.07 ± 0.06	Plateau	Storzer and Wagner (1979)
		0.81 ± 0.16		Florenski et al. (1979)
7. Aouelloul	Glass	$0.16 \pm 0.05, 0.50 \pm 0.16$		Fleischer et al. (1965)
				Fleischer and Price (1967)
		0.46 ± 0.61		Wagner (1966)
		3.25 ± 0.50	Size	Storzer and Wagner (1977)
8. Elgygytgyn	Glass	4.52 ± 0.11	Plateau	Storzer and Wagner (1979)
9. Ries	Glass	15.2 ± 1.6		Fleischer et al. (1965)
		14.8 ± 0.7		Wagner (1966)
		14.6 ± 0.6		Gentner et al. (1967)
		14.6 ± 0.6		Storzer and Gentner (1970)
		14.7 ± 0.3	Plateau	Storzer and Wagner (1977)
	Sphene	14.8 ± 0.4		Wagner (1977)
	Apatite	14.7 ± 0.4		Wagner (1977)
10. Haughton	Apatite	22.4 ± 1.4		Omar et al. (1987)
11. LDG	Glass	37.5 ± 2.4		Fleischer et al. (1965)
		32.1 ± 3.0		Wagner (1966)
		26.6 ± 1.7		Gentner et al. (1969)
		28.5 ± 2.3		Storzer (1971)
		29.4 ± 0.5		Storzer and Wagner (1977)
		28.5 ± 0.8		Bigazzi and De Michele (1996)
12. Popigai	Glass	38.9 ± 2.2	Size	Storzer and Wagner (1977)
		30.5 ± 1.2	Plateau	Storzer and Wagner (1977)
13. Manson	Apatite	61 ± 9		Hartung et al. (1986)
14. Mistastin	Glass	39.6 ± 4.4	Size	Storzer and Wagner (1977)
15. Mien	Glass	92 ± 6	Size	Storzer and Wagner (1977)
16. Boltysh		100 ± 10	Size	Komarov and Raikhlin (1976)
17. Goses Bluff	Apatite + Zircon	134 ± 6		Milton and Sutter (1987)
18. Manicouagan	Glass	208 ± 25		Fleischer et al. (1969b)

(continued)

Impact Glass (Fission Tracks), Table 1 (continued)

Structure	Material	Age (Ma)	Correction techn.	Reference
		200 ± 30	Size	Storzer (1971)
			Size	Storzer and Wagner (1977)
19. Rochechouart	Glass	210 ± 100		Storzer (1971)
		206 ± 39	Size	Storzer and Wagner (1977)
	Apatite	198 ± 25		Storzer and Wagner (1977)
20. Clearwater	Glass	290 ± 30		Fleischer et al. (1969b)
		287 ± 43	Size	Storzer (1971)

When siliceous rocks are present in the target area of a meteorite, the impact produces melting of these rocks. The newly formed glass starts track recording as soon as it cools, and its age is the age of the impact. Glasses are frequently found in impact structures, and most of these structures were dated using glass, that is, an ideal material (homogeneous distribution of uranium, easy etchability) for fission-track dating.

Impact Structures

Ages determined on impact structures by various authors since the early times of fission-track method are shown in Table 1. Location is shown in Fig. 1. Ages are distributed over a long time span, from few 1,000 years up to about 300 Ma. Commonly, ages measured by different authors are in agreement, except in few cases, especially those of the 1960s, probably due to uncertainties on the calibration of the fission-track system. Only in the early 1980s the problem of the calibration of the fission-track system was tackled, and international age standards were identified, in order to

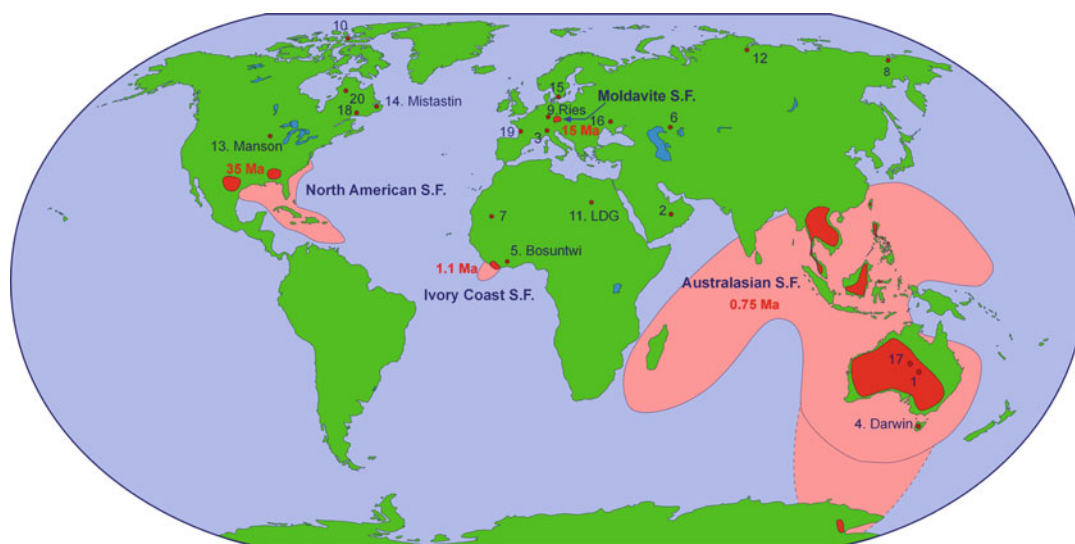


Fig. 1 Location of the terrestrial impact structures dated with the fission-track method (numbers are referred to Table 1). The tektite terrestrial (red) and oceanic (pink) strewn fields with their mean ages are also shown. The dashed strewn field represents the extension of the Australasian s.f. southward to Antarctica, as suggested by recent discovery of microtektite trapped in sediments of the Transantarctic Mountains in northern Victoria Land (Redrawn with modifications after Wagner and Van den Haute (1992))

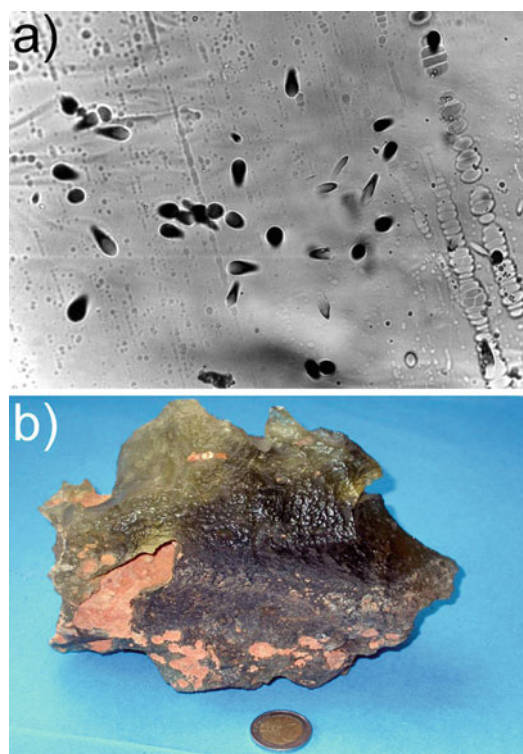


Fig. 2 (a) Fission tracks etched for 240 s in 20 % HF at 40 °C on a polished surface of Libyan Desert Glass; (b) a 2,140 g sample of Libyan Desert Glass “sculptured” and incrustated by the Sahara sand

allow comparison of measurements from different laboratories. The stability of fission tracks in glasses is rather poor: a certain amount of partial annealing occurs also at ambient temperature. For this reason an age on glass is considered a minimum age, even if a technique for correcting thermally lowered fission-track ages – namely, the size correction method or the plateau method – is applied (Storzer and Wagner 1969; Storzer and Poupeau 1973).

Commonly the $\text{Ar}^{40}/\text{Ar}^{39}$ dating method is preferred to fission tracks, substantially for its higher precision, considering that the main component of the experimental error of a fission-track age is related to the number of spontaneous tracks one can count under a microscope. However, in several cases the $\text{Ar}^{40}/\text{Ar}^{39}$ method failed and only fission tracks yielded a reliable age. A significant example is the Libyan Desert Glass (LDG) shown in Table 1 and Fig. 1. Several authors tried to apply the $\text{Ar}^{40}/\text{Ar}^{39}$ method on it but only using fission tracks a reliable age for this glass was obtained (Bigazzi and De Michele 1996 and references therein). This was possible because, due the absence of inclusions, the identification and counting of spontaneous tracks can be performed without uncertainties and for the relatively high areal density – more than 10,000 tracks for cm^2 (Fig. 2a). LDG is a magnificent very pure quartz glass (about 98 %) (Fig. 2b), known since the antiquity, used for tool making during prehistoric times as well as for jewelry in the ancient Egypt. LDG is found in blocks and fragments of various sizes in the Great Sand Sea of the Libyan Desert in Egyptian territory. It is distributed mostly in a relatively large area of the desert, northward in direction of the Mediterranean Sea. Systematic exploration of the Libyan Desert, since the expeditions of Patrick Clayton, in the 1920s and 1930s of the last century, has shown that spreading of LDG is substantially due to anthropic transportation, the original location being in a rather restricted area – few tens of kilometers – relatively close to the Libyan border. LDGs lie on the Cretaceous Nubian basement, along the “corridors,” north–south directed – located in between the



Fig. 3 Samples of Moldavite from different deposits of Bohemia and Moravia (After Bouška 1994)

sand dunes. Origin of LDG was a puzzling issue and various hypotheses were made – sedimentary glass and volcanic glass possibly extraterrestrial – but the most reliable is that LDG is due to melting of the desert sand caused by an impact. However, although various craters have been considered, no correlation of LDG with a specific structure has been found.

Tektites

Tektites are other puzzling natural glasses in our planet that caused long debate since they were described for the first time in 1774 by Count František Josef Kinský as “chrysolites and topazes” and later on, with a scientific approach, by Prof. Josef Mayer at the 1786 meeting of the Czech Academy of Sciences. On the Earth surface four main areas exist – named strewn fields (Fig. 1) – where mysterious glasses are spread, showing an “alien” chemical composition not recalling that one of the sediments where they are found. They have various shapes depending on the history they experienced after they formed – such as reworking of the original sediments, long-distance transportation, and redeposition in younger deposits – meteoric sculpturation. In Fig. 3, samples of the Central European tektites – named Moldavites – are shown, their lengths being between about 3 and 6 cm. Except for the European tektites whose whole strewn field is on ground, the remaining three strewn fields extend in the adjacent Atlantic, Indian, and Pacific oceans where microtektites were discovered in the marine sediments.

Sizes of tektites are relatively small; those of Central Europe do not exceed 300 g of weight and those exceeding 100 g are very rare. Only in Southeastern Asia significantly larger samples were found among the “Muong Nong”-type tektites. Nowadays, the most accepted hypothesis is that tektites have a terrestrial origin and are produced by impacts of heavy extraterrestrial bodies. The high-energy shock wave preceding the meteorite vaporizes the siliceous target rocks, which are

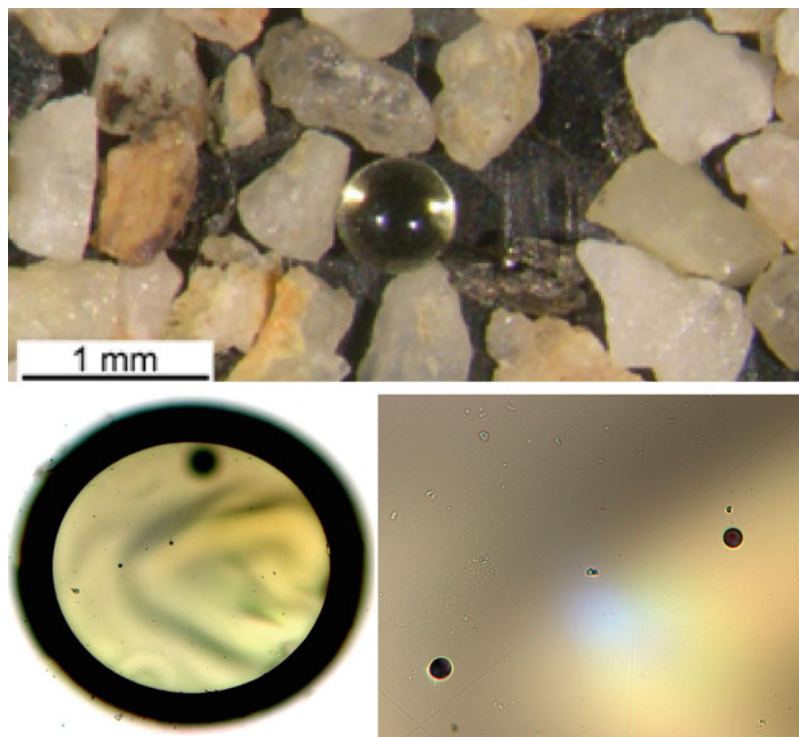


Fig. 4 *Up*: microtektite from the Transantarctic Mountain trapped in fine-grained detritus. *Bottom*: two ^{238}U fission tracks etched for 120 s in 20 % HF at 40 °C in the polished section of a microtektite grain at a magnification of 100× (*left*) and of 500×

ejected in the high atmosphere, and they solidify and fall at distances of 100 and sometimes 1,000 km. In this scenario, comparison of ages of tektites with the age of impact craters, their “potential source,” may result essential for proving the above-described mechanism.

The four strewn fields have well-distinct ages. The oldest tektites are those of the Central American strewn field (age 34.6 ± 0.6 Ma, Storzer and Wagner 1977) which extends in Texas (Bediasites) and Georgia (Georgirites) – in the continent – and in the Caribbean Sea. Although various impact structures of the American continent have been studied, no correlation with these tektites was found. The next strewn field is the Central European one. Moldavites are found in deposits of various ages, since Middle Miocene, Pliocene, and Pleistocene in South Bohemia and Moravia up to Holocene in Elba riverbanks. The fission-track age of Moldavite, 14.7 ± 0.4 Ma (Wagner 1966; Storzer and Wagner 1977), is the same determined by the same authors for the Ries crater (Table 1) located in Bayer, Germany. This represents an important confirmation of the terrestrial origin of tektites and of the formation model described above. Moldavite is an excellent glass, with relatively high-track densities, without defects that might produce “spurious” tracks, so fission-track identification during counting is unequivocal. In addition, many age determinations obtained by several authors using also K-Ar and $\text{Ar}^{39}/\text{Ar}^{40}$ are available. For these reasons it has been distributed as reference material for fission-track dating in glass (Balestrieri et al. 1998). The next Ivory Coast tektites are significantly younger (1.08 ± 0.10 Ma, Storzer and Wagner 1977), confirming the rarity of the event responsible for the formation of these glasses. Also in case of this strewn field, an associated impact structure was identified, i.e., the Bosumtwi crater located in Ghana (1.04 ± 0.11 Ma, Table 1). The youngest strewn field, the Australasian, is the largest one. It extends in Southeastern Asia and Australia and in the Indian and Pacific Ocean. These tektites have been named Indochinites, Javanites, Philippinites, Billitonites, and Australites, according to the

area where they were found. Their age (0.71 ± 0.07 Ma, Storzer and Wagner 1977; 0.693 ± 0.025 Ma, Storzer and Wagner 1980; 0.77 ± 0.08 Ma, Bigazzi and De Michele 1996) is in agreement with the age of the Darwin crater in Tasmania (0.74 ± 0.04 Ma, Table 1), but this crater is relatively small (ca. 1 km), so it is highly unlikely that it could have been the source of such extended strewn field. All the known Asian craters, potential sources of the Australasian strewn field, have been considered, but none of them shows an age consistent with the tektites. In addition, it has been also hypothesized that this large strewn field may have been produced by more than one impact: Storzer and Wagner (1980) determined for some Australian tektites ages older (0.830 ± 0.028 Ma) than those of Southeastern Asia cited above. Therefore, this topic needs further investigation.

A recent research has shown that the Australasian strewn field might be even more extended than expected. Microtektites were recently discovered on the Victoria Land Transantarctic Mountains (Fig. 4). They were found trapped in the fine-grained local detritus accumulated in weathering pits of the glacially eroded summits of Miocene age known as Transantarctic Mountain micrometeorite traps (Folco et al. 2008). Petrographic studies, major and trace element compositions, Sr and Nd isotopic compositions, and a low-resolution, yet Quaternary, $^{40}\text{Ar}/^{39}\text{Ar}$ age of 0.76 ± 0.98 Ma suggested that these microtektites most likely represent a major southern extension of the Australasian tektite strewn field. In order to better constrain the formation age of Transantarctic Mountain microtektites, their fission-track age was determined. The obtained fission-track plateau age of 0.85 ± 0.17 Ma, although affected by a relatively large experimental error due to the low number of counted spontaneous tracks owing to the small surface suitable for the analysis, is well consistent with the ages determined for the Australasian tektites.

Summary and Conclusions

Impacts of large meteoritic bodies with the Earth ground in presence of siliceous rocks may produce impact glasses through melting. By dating these glasses, one obtains the age of the related impact events. Since the early days of the fission-track method, various attempts have been successfully made in order to date impact glasses that usually are ideal material where to apply this technique as most of them show a relatively high number of tracks that can be unequivocally identified. Although the fission-track method usually relies lower precision ages in comparison with other radiometric methods, its application supplied precious information for correlating – or for excluding correlation – of impactites with specific craters and for reconstructing tektite strewn fields. Impressive examples of the performance of fission tracks in this field are those quoted above of the Libyan Desert Glass and of the Antarctic microtektites. This method produced unique efficacious data where other techniques failed.

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Magnetic Anomalies

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Definition

A magnetic anomaly is the magnetic field remaining after the Earth's magnetic field has been removed from the observed amplitude of the local magnetic field. The remanent magnetization of rocks records past variations of the geomagnetic field whereby spatial changes in their magnetization give rise to magnetic anomalies. We can date the oceanic crust by studying the unique pattern of lineated positive and negative magnetic anomalies that arise due to past reversals of the geomagnetic field with known age. Besides the primary signal that is related to past polarity reversals, the shape and tiny variations (wiggles) of the anomalies can be used to further constrain the age of the crust. Altogether, magnetic anomalies provide the main source of dating for the oceanic basins and lay the foundations for global plate reconstructions which place important constraints on the development of the lithosphere, biosphere, hydrosphere, cryosphere, and global climate.

Introduction

The Earth's magnetic field (the geomagnetic field) is generated by convection motions in the liquid outer core. The field is not steady but varies with time due to the dynamic of motions within the outer core leading to the ever-changing strength and position of its poles. In extreme cases and in irregular occurrences, hundreds of rapid reversals in the polarity of the field have taken place (Amit et al. 2010). The direction and strength of the geomagnetic field may get permanently imprinted into iron-rich rocks during their formation. The resultant remanent magnetization gives rise to local magnetic fields that generate "magnetic anomalies." Although continental magnetic anomalies may, in certain circumstances, provide some age constraints on the magnetized rocks, it is the marine magnetic anomalies that have crucial implications for the dating of the oceanic crust and serve as the basis for the Mesozoic and Cenozoic global plate reconstruction models (e.g., Seton et al. 2012).

The oceanic crust is formed along mid-ocean ridges, where melt rises and cools to form the crust (Vine and Matthews 1963). The cooling crust becomes magnetized in the direction of the geomagnetic field and retains magnetization proportional to its strength. After initial formation, the newly formed crust moves away and ages progressively from the ridge in a process known as seafloor spreading. In that way, a symmetric and unique magnetization pattern is formed across the spreading ridges. Although the oceanic crust is formed in a complex accretion process that varies in space and time, a remarkably consistent pattern of lineated anomalies are found globally (Maus et al. 2009). This pattern of anomalies predominantly reflects past reversals of the dipolar geomagnetic field and has been calibrated with radioisotopic age control at certain tie points, or astronomical cyclicity in stratigraphic sections, to form the basis for the geomagnetic polarity timescale (GPTS, Cande and Kent 1995; Channell et al 1995). Comparison of the predicted pattern of anomalies (based on

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the GPTS and a simple two-dimensional magnetic structure) with the observed marine magnetic anomalies (for example see Fig. 1) allows researchers to globally map lines of equal and known age (i.e., isochrones) (Fig. 2).

Magnetic Anomaly Data and Their Physical Properties

The collection of marine magnetic data is traditionally made with magnetometers that measure the magnitude of the magnetic field. To avoid contamination of the signal by the survey platform (e.g., submarine vehicles, ships, helicopters, and airplanes), the magnetometers are usually towed some distance away from the towing platform. The measured values are the summation of the strength of the present-day geomagnetic field and the magnetic fields induced by the igneous crust in the direction of the geomagnetic field. The contribution of the geomagnetic field is computed and subtracted from the total value using the appropriate International Geomagnetic Reference Field model (e.g., Finlay et al. 2010). Minor additions are induced by external magnetic fields but these are usually rather negligible and contain shorter wavelengths as compared to the typical geological signature. These additions can be accounted for using gradiometer data or data collected in a reference magnetic base station. Modern magnetometers have an absolute accuracy of ~ 1 nanotesla (nT), which is two to three orders of magnitude smaller than the target magnetic anomalies.

The shape of a magnetic anomaly depends on the orientation of the spreading axis, the direction of the ambient geomagnetic field, the magnetization direction of the source rocks, and the shape of the magnetic boundaries. Therefore, in most places, the anomalies are skewed and spatially shifted from the actual location of the magnetization contrasts that generate them. To assign an accurate location for each of the magnetic contrasts with known age, it is essential to take into consideration the various parameters affecting the shape of the anomalies through a comparison against a two-dimensional forward magnetic modeling computed with the appropriate parameters (Blakely 1995 and Fig. 1). The resultant magnetic anomaly picks (Fig. 2) delineate isochrons of the igneous oceanic crust. These isochrons, found on both sides of the spreading ridges, together with fracture zone locations, provide the basis for the computation of relative motions between adjacent plates and serve as the basis for the construction of global plate reconstruction models.

Outstanding Issues

Marine magnetic anomalies have outstanding issues that stem from the physical principles that govern their formation and from limitations that relate to the recorded geomagnetic field. In the equatorial region, where spreading ridges are oriented in a north–south direction parallel to the direction of the geomagnetic field, no obvious (i.e., large amplitude) magnetic anomalies exist. Hence, locating magnetic anomalies there is virtually impossible, leading to the absence of accurate age models for the equatorial Atlantic and Pacific (Fig. 2). Oriented three-axial magnetometers that measure the components of the anomalous field allow the detection of the magnetization boundaries with better confidence (Gee and Cande 2002). Although efforts have recently been made to constrain the age of the oceanic crust in certain equatorial regions (Barckhausen et al. 2013, 2008), the age of the oceanic crust there remains poorly defined and is the focus of geophysical investigations.

Thus far, dating of the oceanic crust has been based on reversals-related anomalies. Therefore, the spatial resolution of which magnetic anomalies can date the crust depends on past reversal frequency

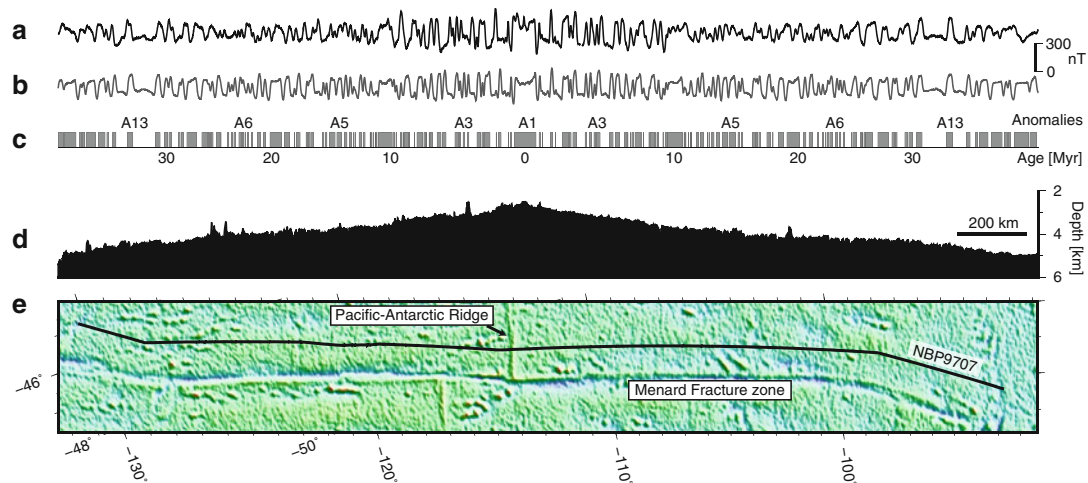


Fig. 1 A representative magnetic anomaly profile (NBP9707 cruise) across the Pacific–Antarctic Ridge. **(a)** Observed magnetic anomalies along the NBP9707 track. The synthetic magnetic anomaly profile **(b)** is calculated based on the geomagnetic polarity timescale of Cande and Kent (1995) where the positive chrons used are shown in the bar graph **(c)**. The numbers beneath the graph are ages (in millions of years) and the key polarity chrons are identified above the graph. The forward synthetic model uses this polarity pattern in a 0.5-km-thick source layer that has a mean magnetization of 10 Am^{-1} . Spreading rates that were used to construct the model follow Croon et al. (2008). Seafloor depth **(d)** was used as the *top* of the magnetic source layer. The location of the NBP9707 track is shown in panel **(e)**, projected on top of a satellite-derived free-air gravity anomaly map (Sandwell and Smith 2009)

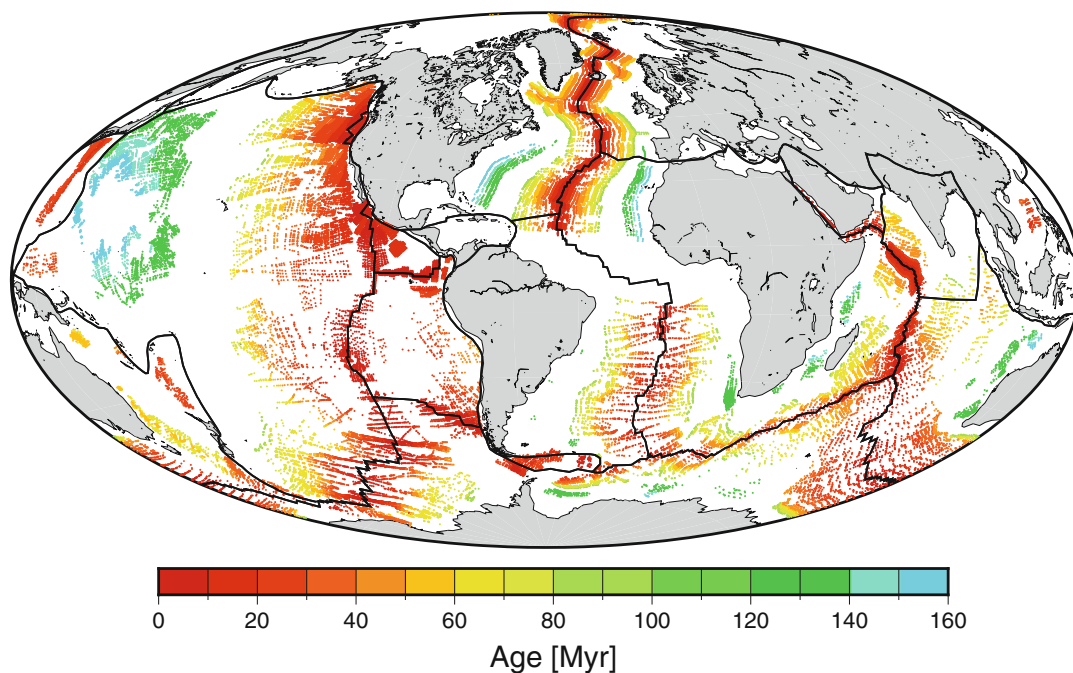


Fig. 2 Identified locations of marine magnetic anomalies with known age (compiled by Seton et al. 2014). Note the absence of identifications in the equatorial regions and in the Cretaceous quiet zones

of the geomagnetic field. Periods that had frequent reversals, such as during the Cenozoic period, allow for the construction of well-constrained crustal age models (Fig. 2). However, during the Cretaceous period, the reversal frequency of the geomagnetic field was low (less than once every million years), with the extreme case of the Cretaceous Normal Superchron that lasted between

121 to 83.5 million years ago (Cande and Kent 1995; He et al. 2008). Therefore, the age of the crust that was formed during the superchron period (termed “quiet zone,” Fig. 2) remains poorly resolved. Luckily, past fluctuations in the intensity of the dipolar geomagnetic field are also recorded by the magnetized rocks, resulting in globally correlatable wiggles found between the primary, reversals-related magnetic anomalies (Bouligand et al. 2006; Cande and Kent 1992; Gee et al. 2000; Granot et al. 2012). Ongoing efforts are being made to refine the existing crustal age models using these magnetic wiggles as a means to establish internal isochrones between the primary anomalies.

Remanent magnetization directions of the magnetic source layer influence the shape of magnetic anomalies. Therefore, if a plate drifted during its geological history in a known fashion, one could potentially utilize the predicted remanent magnetization directions to constrain the age of the crust. “Paleomagnetic poles,” the magnetic poles of a certain plate, are calculated from independent paleomagnetic sites with known ages (see entry “Palaeomagnetism, Continental Drift”). These poles place constraints on past motions of the plates, thereby allowing the prediction of the directions of magnetization for every location on a given plate. Forward modeling of the expected magnetic anomalies for different periods of time based on the paleomagnetic poles of the appropriate plate until a reasonable match is found provides a crude, yet important, age constraint on the source rocks. This methodology may, under certain conditions, help to constrain the age of continental magnetic anomalies.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Continental Drift \(Palaeomagnetism\)](#)
- ▶ [Magnetometer](#)
- ▶ [Milankovitch Cycles](#)

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Meteorites (Lu–Hf)

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Definition

Radiogenic dating of meteorites and tracing of planetary differentiation using the radiogenic decay of ^{176}Lu to ^{176}Hf and variations in their isotopic abundances.

Introduction

The ^{176}Lu – ^{176}Hf radiogenic isotopic system (^{176}Lu half-life ~ 37 Ga) is a powerful chronometer and tracer of geochemical processes and planetary evolution. It was formerly assumed that the Lu–Hf system would be a valuable complement to the short-lived (^{146}Sm – ^{142}Nd with a ~ 68 Ma half-life) and long-lived (^{147}Sm – ^{143}Nd with a ~ 106 Ga half-life) Sm–Nd radiogenic systems. The Lu–Hf and Sm–Nd systems involve refractory and lithophile elements, all of which have mostly incompatible behavior (e.g., Patchett and Tatsumoto 1980; Boyet and Carlson 2005; also see entry on “► [Samarium–Neodymium, Dating](#)” for further details). The Lu–Hf pair has an advantage over the Sm–Nd pairs in that it includes two elements with distinct chemical behaviors: Lu is a heavy rare-earth element (REE) and Hf is a high field strength element (HFSE). Elemental fractionation between Hf and Lu is consequently greater in geological systems than for two REEs that have similar chemical behavior.

There has been tremendous progress made over the last few years for measuring Lu and Hf isotopic abundances with the development of multi-collector inductively coupled plasma mass spectrometry techniques (MC-ICP-MS). Such technical advances have led to the collection of enormous volumes of high-precision Hf isotopic data over the last 15 years. By measuring precisely small variations in the abundance of ^{176}Hf in various minerals and rocks with different Lu/Hf (parent/daughter) ratios, we can now date, with ~ 1 – 10 % precision, geological, and extraterrestrial processes as recent as ~ 15 Ma in igneous, metamorphic, or sedimentary rocks. Many recent studies have been focused on understanding the differentiation of the mantle and crust, and the dynamics of these reservoirs on the Earth, Moon, Mars, and planetesimals (e.g., Vervoort et al. 1996; Blichert-Toft et al. 1999, 2002). Studies in igneous geochemistry and metamorphic petrology particularly benefit from minerals that highly fractionate Lu from Hf during geological processes. Such minerals include zircon and ilmenite with very low Lu/Hf to track crustal evolution, and garnet and phosphate with very high Lu/Hf, to establish the chronology of metamorphic events. These accessory minerals are nevertheless rare in extraterrestrial materials, which sample primitive, ultramafic, and rarely evolved planetary crust. Also, because of the low concentration levels of Hf and REE in meteorites and limited supplies of these precious planetary materials, most of the cosmochemical studies have been focusing on bulk-rock analysis. Occasionally, silicate separates such as pyroxene, feldspar series, and olivine (Bouvier et al. 2008a; Thrane et al. 2010) oxides (e.g., chromite; Lapen

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et al. 2010), and phosphates (Amelin 2005) have been analyzed for chronological studies of meteorites.

One area of considerable activity in geochemistry is the isotopic analysis of Hf in parallel with U–Pb zircon studies, either to constrain early crustal growth and evolution or as a complement to detrital zircon studies (e.g., Harrison et al. 2005). Interpretation of these data, however, relies on the availability of unambiguous and well-constrained decay constants for these isotope systems. At the moment, a major issue for deciphering planetary differentiation processes is that the apparent ages deduced from the Lu–Hf isochron method in planetary materials are variable by ~5 %. Consequently, there is an uncertainty for estimates of the initial Hf isotopic composition of the solar system and consequently an even larger uncertainty for the Earth’s bulk composition. The following sections detail the recent determination of the ^{176}Lu – ^{176}Hf parameters for solar system evolution and potential building blocks of the Earth. A third section discusses the recent findings of irradiation effects on Hf isotopes due to the long-term exposure of planetary materials to cosmic rays in space and how it affects the interpretation of Lu–Hf and Sm–Nd systematics in many meteorites and lunar samples. Finally, the last section will present Lu–Hf chronological studies for Martian meteorites, which are not affected by these processes and can therefore be used to constrain the formation times of these rocks.

Lu–Hf Isotopic Composition of the Solar System

The β^- decay of 176-Lutetium (^{176}Lu ; 2.56 % of Lu) produces 176-Hafnium (^{176}Hf ; 5.26 % of Hf). Dixon et al. (1954) reported that ^{176}Lu also decays by electron capture to ^{176}Yb with a branching ratio of ~3 %. Determinations of the ^{176}Lu decay constant ($\lambda^{176}\text{Lu}$) by physical counting experiments vary widely, leading geochemists to use the Lu–Hf isochron method in various meteoritic and geological samples of known U–Pb ages (see Albarède et al. 2006 for a review). This method deduces the value of the decay constant λ from the slope s of the isochron of an object of known age t by the relationship $s = e^{\lambda t} - 1$ (Fig. 1). An important requirement is that both systems closed rapidly to diffusion and remained subsequently undisturbed.

An unsolved discrepancy of ~5 % exists between the determinations of $\lambda^{176}\text{Lu}$ (and consequently Lu–Hf ages) based on meteorites at $\sim 1.93\text{--}1.99 \times 10^{-11} \text{ year}^{-1}$ (e.g., Patchett and Tatsumoto 1980; Blichert-Toft et al. 2002; Bizzarro et al. 2003; Thrane et al. 2010) and those based on terrestrial samples at $1.867 \times 10^{-11} \text{ year}^{-1}$ (Scherer et al. 2001; Söderlund et al. 2004). It was suggested that this difference was caused by an early episode of irradiation in the solar system that generated ^{176}Hf excesses in chondrite, eucrite, and angrite meteorites (Albarède et al. 2006; Thrane et al. 2010; Fig. 1). This effect, however, is not observed by the time of formation of phosphates from ordinary chondrite (4,551 Ma) and acapulcoite (4,557 Ma) meteorites (Amelin 2005). This discrepancy hampers accurate determination of the initial Hf isotopic composition of the solar system and the Earth, leading to an uncertainty of as much as seven epsilon Hf units for the composition of the modern BSE (denoted εHf , expressed as the deviations in parts per ten thousand relative to the reference CHUR parameters) (Fig. 1).

There are now several additional Lu–Hf isotopic datasets on bulk chondrites that have been gathered using MC-ICPMS since the pioneering work by Blichert-Toft and Albarede (1997). When comparing metamorphosed (petrologic types 4–6) and unmetamorphosed (petrologic types 1–3) chondrites, it is evident that there is a disturbance of the Lu–Hf bulk chondrite isochron during thermal metamorphism on the chondrite parent body. Metamorphism on chondrite parent bodies is the consequence of accretionary and radiogenic heat that lasted for at least 10–100 Ma on planetesimals with tens of kilometer diameters. Later planetary impacts may also have contributed to such

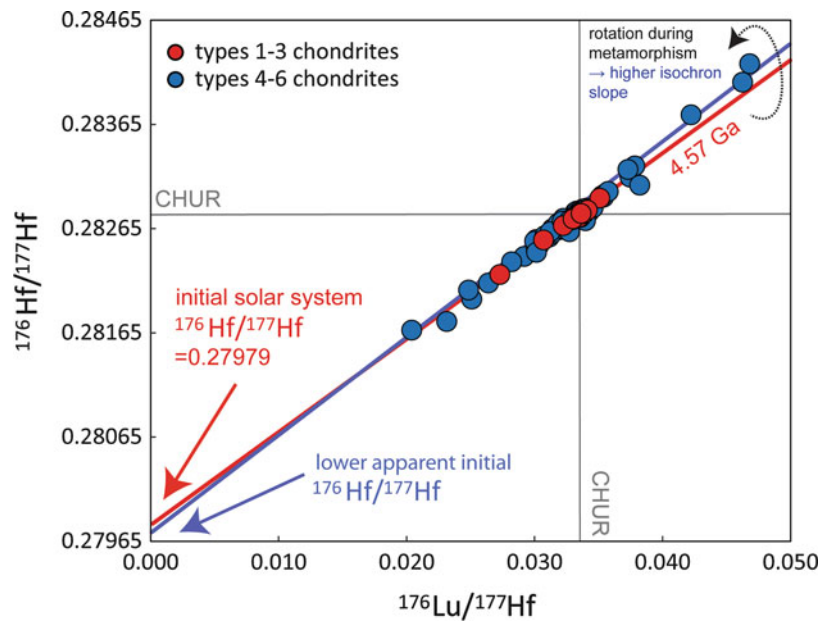


Fig. 1 Lu–Hf compositions of unmetamorphosed (petrologic types 1–3, *red symbols*) and metamorphosed (petrologic types 4–6, *blue symbols*) bulk chondrites obtained using efficient dissolution methods (Bizzarro et al. 2003; Patchett et al. 2004; Bouvier et al. 2008b; Dauphas and Pourmand 2011) with corresponding isochron regression lines. Thermal metamorphism produces a redistribution of Lu relative to Hf on the chondrite parent bodies and consequently a rotation and larger spread of the Lu–Hf compositions of the petrological types 4 to 6 bulk chondrites. Proposed initial solar system, and modern CHUR and BSE compositions are also indicated (Bouvier et al. 2008b); see text for additional details

disturbances at depth in the planetary bodies. Recently determined internal Lu–Hf isochrons of individual refractory inclusions (4,568 Ma) and chondrite, eucrite and angrite meteorites also show variability in the deduced $\lambda^{176}\text{Lu}$ values and initial Hf isotopic compositions, showing that secondary processes such thermal metamorphism and impact must have heterogeneously affected the parent bodies of these meteorites.

Building Blocks of the Earth

Because the Lu–Hf and Sm–Nd systems involve refractory and lithophile elements, it has been always assumed that the average composition of bulk terrestrial planets should be the same as that of primitive chondrites, and for this reason, the term Chondritic Uniform Reservoir was defined (CHUR). Knowing the bulk composition of the Earth is essential for these isotopic tools to realize their potential in planetary studies. The starting composition of terrestrial planets (e.g., Earth, Mars) is commonly assumed to be chondritic for Lu–Hf and by extension for Sm–Nd, which are both refractory elements. There are nevertheless variations in stable isotopic compositions of many elements that show that the Earth is made of different types of chondritic and unknown planetary materials such as potentially differentiated materials and comets.

The hypothesis of collisional erosion during accretion and differentiation would lead to fractionated bulk composition of planets. This mechanism was suggested to explain the so-called missing reservoir for the Earth or super-chondritic composition (Boyet and Carlson 2005; Caro et al. 2008; O'Neill and Palme 2008), but such fractionation and missing component is nevertheless not observed for large ~400 km diameter planetesimals such as 4 Vesta, the accepted parent body of basaltic eucrite meteorites

which have near-chondritic Lu–Hf compositions (Blichert-Toft et al. 2002). Evidence from lunar Lu–Hf and Sm–Nd isotopic compositions also suggests that the chondritic model holds for these two systems for the Moon and consequently also for the Earth (Sprung et al. 2013).

Lu–Hf Isotopic Variations in Meteorites

The improvements made on the precision of isotopic measurements allow scientists to generate new insights into the origin of isotopic variation and the stellar contribution (e.g., giant stars, supernovae) to the matter present in the solar system (e.g., Carlson et al. 2007). Some isotopes of interest (e.g., ^{178}Hf , ^{152}Sm , ^{146}Nd) can also be affected by neutron capture which is a quite common process in meteorites and planetary materials (e.g., lunar rocks) due to their journey into space or long-term exposure on planetary surfaces. If there are large isotopic anomalies due to cosmic-ray exposure on the normalizing isotopes, it will ultimately result in incorrect normalizations of all the ratios used for Lu–Hf dating.

Nucleosynthetic anomalies. It was suggested that Lu and Yb isotopic variations could potentially explain discrepancies in the ^{176}Lu decay rates deduced in meteorites if there were detectable irradiation effects for Lu or a branching decay of ^{176}Lu to ^{176}Yb (Amelin and Davis 2005; Scherer et al. 2005). $^{175}\text{Lu}/^{176}\text{Lu}$ ratios have been measured in planetary materials and do not show any resolvable variations that could explain such discrepancy (Wimpenny et al. 2013). For Hf, Sprung et al. (2010) show that there is no resolvable variation in the stable isotopic composition of bulk chondrites (Sprung et al. 2010), while small variations in leached chondrites (Qin et al. 2011) and refractory inclusions (Akram et al. 2013; Bouvier and Boyet 2013) were most recently found and likely caused by nucleosynthetic anomalies but are too small to affect Lu–Hf dating of meteorites.

Irradiation effects. The Lu–Hf dating of meteorites can be significantly affected by variations in stable isotopic abundances for Lu and Hf isotopic compositions due to irradiation effects from cosmic-ray exposure. The isotope ^{149}Sm is very useful as it has a large thermal neutron capture cross section and can be used to monitor irradiation effects on isotopic compositions (e.g., Lingenfelter et al. 1972). For example, it has been used for correcting irradiated Nd isotopic compositions of lunar samples (Nyquist et al. 1995). Secondary neutron capture effects on Hf isotopes have been detected in some achondrites (mesosiderites, aubrites) and lunar samples (Sprung et al. 2010) and were corrected using the measured $^{149}\text{Sm}/^{144}\text{Sm}$ ratio of the meteorites. These findings have changed the view of Hf–Nd isotopic evolution and differentiation of the lunar mantle and crust and also provided an additional constraint on the validity of the chondritic model for the Hf–Nd isotopic system for the Moon and by extension the Earth (Sprung et al. 2010).

Lu–Hf Dating Martian Meteorites

Martian meteorites are the only meteorites not affected by nucleosynthetic anomalies and irradiation effects that affect most of the planetary materials, as described in the previous sections. There has been extensive geochemical and chronological research on Martian meteorites as more than 150 individual specimens have been found so far. Using Lu–Hf chronometry, the unique orthopyroxenite Allan Hills 84001 (found in 1984 in Antarctica) has been dated at 4.1 Ga (Lapen et al. 2010) consistent with its Pb–Pb age (Bouvier et al. 2009), while shergottites show a broad range of Lu–Hf ages from about 185 Ma for Zagami (fell in 1962 in Nigeria) (Bouvier et al. 2005) to 580 Ma for Tissint (fell in 2012 in Morocco) (Grosshans et al. 2013) contrasting with their

corresponding Pb–Pb ages of 4.1 Ga and 4.3 Ga, respectively (Bouvier et al. [2008a](#)). The explanation for why only the Lu–Hf ages of shergottites are much younger than their corresponding Pb–Pb ages is an intensive area of current research. It is good to note that shergottite meteorites have been extremely shocked by impact on the surface of Mars and contain abundant impact melt and high-pressure polymorphs of many minerals (maskelynite replacing plagioclase, stishovite replacing quartz, ringwoodite replacing olivine). These observations may explain why Lu–Hf and other similar parent-daughter radiogenic isotopic chronometers have been disturbed in these meteorites (El Goresy et al. [2013](#)).

Summary or Conclusions

The most accurate value for $\lambda^{176}\text{Lu}$ deduced from geological materials is $1.867 \times 10^{-11} \text{ year}^{-1}$ with a corresponding half-life of 37.1 Ga. There is no robust evidence for an accelerated decay of ^{176}Lu in meteorites. The calculated initial ratio of $^{176}\text{Hf}/^{177}\text{Hf} = 0.27979$, as deduced from the modern CHUR parameters of $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$ and $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$, remains the best estimate for the initial isotopic composition of the solar system. The Lu–Hf system is extremely useful for tracking early planetary processes and chemical reservoirs formed in the interior of planets. Its chronological applications to meteorites are nevertheless limited due to its lower precision (a few million years to tens of millions years) and higher susceptibility to disturbance compared to the Pb–Pb chronometer, which is the most accurate and precise absolute chronometer used to establish the time scales of formation of meteorites, planets, and solar system (see entry on “► [Uranium–Lead, Extraterrestrial, Planetary Materials](#)”).

Cross-References

- [Geochronology](#)
- [Lutetium–Hafnium Dating](#)
- [Lutetium–Hafnium, Meteorites](#)
- [Samarium–Neodymium, Meteorites](#)
- [Samarium–Neodymium Dating](#)
- [Meteorites \(U–Pb\)](#)

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Meteorites, Rubidium–Strontium, and Samarium–Neodymium Chronology

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Rb–Sr Chronology of Meteorites

Rb–Sr Isotopic Systematics

The Rb–Sr isotopic system has been used to constrain the evolution of Solar System since it was first applied to basaltic achondrite meteorites by Papanastassiou and Wasserburg (1969). Although this method was first used to obtain an age by Hahn et al. (1943), it was not until Nier-type mass spectrometers (see entry “► [Mass Spectrometers](#)”) were readily available that it came into widespread use. The principles of the Rb–Sr system and its application to geologic materials are discussed by several authors (e.g., Dickin 2005; Faure 1998; see entry “► [Rb–Sr Dating](#)”) and are not reiterated here. However, it is important to understand that Rb–Sr ages are based on the isochron method in which several aliquots, usually separated mineral fractions, of a sample are analyzed for $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and then plotted on an isochron diagram. The slope of a regression line through the data defines the age of the sample, and the y intercept defines the initial Sr isotopic composition of the fractions at the time they formed from a common source. Uncertainty in the ages is based primarily on the scatter of the data points on the isochron diagram. Ages determined from this method are only valid if the aliquots that define the isochron regression were in isotopic equilibrium when they formed. Thus, the age records the time elapsed since the aliquots shared a common Sr isotopic composition. This is usually considered to be when the minerals crystallized from a magma.

In order to obtain an age from the slope of the isochron, the ^{87}Rb decay constant must be known. Unfortunately, the decay of ^{87}Rb to ^{87}Sr is a low-energy transformation of only 275 keV, involving the emission of a beta particle and an antineutrino ($_{37}^{87}\text{Rb} \rightarrow _{38}^{87}\text{Rb} + \beta + \nu^- + Q$), and is therefore difficult to measure accurately. As a result, meteorite Rb–Sr ages have been calculated using several decay constants ranging from $1.39 \times 10^{-11} \text{ year}^{-1}$ to $1.42 \times 10^{-11} \text{ year}^{-1}$ (Aldrich et al. 1956; Steiger and Jäger 1977). Ages reported in the literature must therefore be adjusted to a common decay constant for comparison. After a detailed analysis of published ^{87}Rb decay constants, Begemann et al. (2001) suggested using the value of $1.402 \times 10^{-11} \text{ year}^{-1}$ determined by Minster et al. (1982) and Shih et al. (1985). This is the value most commonly used for meteorite and lunar chronology studies today. Another factor that must be considered when examining Rb–Sr data in the literature is the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values obtained on standards. This is complicated by the fact that early investigations used different strontium isotopic standards, such as seawater or plagioclase separated from meteorites. In the mid-1970s, the NBS-987 standard became widely used, and individual laboratories often normalized their data to the certified $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71014. More recently, the consensus of the Rb–Sr isotope community is that $^{87}\text{Sr}/^{86}\text{Sr}$ value of this standard is 0.71025. In this discussion, all $^{87}\text{Sr}/^{86}\text{Sr}$ data are renormalized to this $^{87}\text{Sr}/^{86}\text{Sr}$ value, and Rb–Sr ages are recalculated using an ^{87}Rb decay constant of $1.402 \times 10^{-11} \text{ year}^{-1}$.

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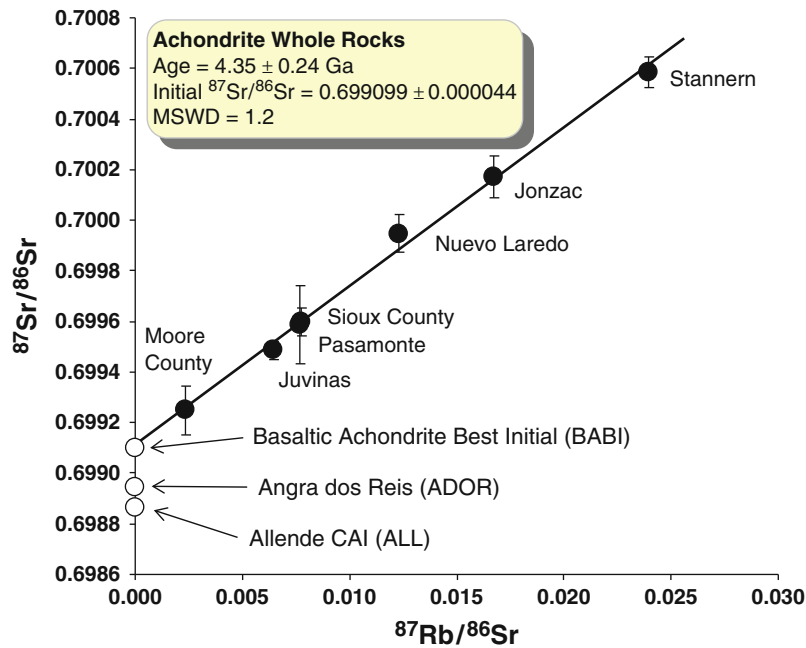


Fig. 1 A Rb–Sr isochron diagram of achondrite meteorite whole rock analyses replotted from data of Papanastassiou and Wasserburg (1969)

Chondrites, Angrites, and Eucrites

Ideally the slope of a regression line constructed to pass through a suite of whole rock and/or mineral fractions, and typically shown on a Rb–Sr isochron diagram, is used to constrain the age of a sample. In some cases, ancient Rb–Sr ages have been obtained for individual basaltic achondrites, such as Ibitira and Juvinas (Allègre et al. 1975; Birck and Allègre 1978), which record the crystallization age of the sample. However, many meteorite samples either have limited internal variation in $^{87}\text{Rb}/^{86}\text{Sr}$ or demonstrate evidence for significant disturbance of the Rb–Sr system by secondary processes occurring on their parent bodies or on Earth. To address these problems, ages of individual samples have been calculated from an assumed initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. In one of the first investigations of meteorite samples, Papanastassiou and Wasserburg (1969) measured Rb–Sr in a group of basaltic achondrites obtaining an age of 4.35 ± 0.24 billion years (Ga) and an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.699099 ± 0.000044 (Fig. 1). This is a whole rock isochron and is based on the premise that all the analyzed meteorites are derived from a common source region at the same time. As such, the initial Sr isotopic composition determined from the isochron records the value of the source region. This initial value is known as BABI (Basaltic Achondrite Best Initial) and is used as a reference point for model ages calculated from the Rb–Sr isotopic compositions of other meteoritic samples. BABI model ages have proven invaluable in constraining the relative age of the earliest meteorite samples (e.g., Papanastassiou 1970) due to the disturbed nature of their Rb–Sr isotopic systematics.

A summary of initial $^{87}\text{Sr}/^{86}\text{Sr}$ values from the most ancient meteorite samples is presented in Table 1. From this table, it is apparent that BABI is not the least radiogenic Sr isotopic composition measured in the Solar System. This reflects the fact that other meteorite samples, such as calcium–aluminum–rich inclusions (CAIs) from carbonaceous chondritic meteorites and angrite meteorites, are older than the basaltic achondrites. The initial Sr isotopic compositions measured by Gray et al. (1973) of these samples were given acronyms as follows: Allende (ALL) and Angra dos Reis

Table 1 Initial Sr isotopic compositions of ancient samples

Sample	Measured initial $^{87}\text{Sr}/^{86}\text{Sr}$	Normalized initial $^{87}\text{Sr}/^{86}\text{Sr}^a$	Reference
Allende CAI D7 ($\equiv$ ALL)	0.69876 ± 0.00004	0.69887 ± 0.00004	Gray et al. (1973)
Allende CAI N17	0.69861 ± 0.00004	0.69872 ± 0.00004	Tatsumoto et al. (1976)
Allende CAI 3529-30	0.69885 ± 0.00002	0.69891 ± 0.00002	Podosek et al. (1991)
Allende CAI A13S4	0.69894 ± 0.00001	0.69894 ± 0.00001	Marks et al. (2013)
Chondritic meteorites	0.69885 ± 0.00001	0.69895 ± 0.00001	Minster et al. (1982)
Angra dos Reis ($\equiv$ ADOR)	0.69884 ± 0.00004	0.69895 ± 0.00004	Papanastassiou (1970)
Angra dos Reis	0.69897 ± 0.00002	0.69897 ± 0.00002	Nyquist et al. (1994)
LEW 86010	0.69897 ± 0.00001	0.69897 ± 0.00001	Nyquist et al. (1994)
Basaltic Achondrites ($\equiv$ BABI)	0.69899 ± 0.00004	0.69910 ± 0.00004	Papanastassiou and Wasserburg (1969)
Basaltic Achondrites	0.69899 ± 0.00004	0.69909 ± 0.00004	Birck and Allègre (1978)

^aData normalized to NBS-987 = 0.71025. Initial isotopic compositions calculated from isochron or least radiogenic sample using of $\lambda^{87}\text{Rb} = 1.402 \times 10^{11} \text{ year}^{-1}$. More significant figures are often available from original references

(ADOR). Subsequent measurements on the same sample types are often slightly different than the original values and are listed separately in Table 1.

Martian Meteorites

Whereas obtaining internal Rb–Sr isochron ages for the most ancient meteorites has often proven to be a difficult task, defining Rb–Sr ages for young meteorites from differentiated bodies, such as Mars and the Moon, has been less difficult. The first unequivocal young Rb–Sr date was determined for the meteorite Nakhla, which belongs to the SNC (shergottite-nakhlite-chassigny) group of meteorites. Ages of $1.30 \pm 0.02 \text{ Ga}$ and $1.23 \pm 0.01 \text{ Ga}$ were determined by Papanastassiou and Wasserburg (1974) and Gale et al. (1975). Young ages of 163–178 million years (Ma) were later obtained on the related Shergotty and Zagami meteorites by Nyquist et al. (1979a) and Shih et al. (1982). Initially the young ages obtained on the SNC meteorites were interpreted to reflect isotopic re-equilibrium associated with extensive metamorphism of their parent body. The extent of metamorphism required to reset the Rb–Sr system led Nyquist et al. (1979b) to conclude that the parent body was very large and likely to be the planet Mars. Later petrologic work (Jones 1986) and isotopic analysis involving the Sm–Nd chronometer (Borg et al. 1997) demonstrated that the ages most likely recorded a crystallization event rather than a metamorphic event. Numerous Rb–Sr (and Sm–Nd) ages have now been obtained of the SNC suite of Martian meteorites. The shergottites define 4 general age groups of ~170 Ma, ~330 Ma, ~475 Ma, and ~575 Ma (see summaries by Nyquist et al. 2001a; Borg and Drake 2005). Several additional nakhlites have also been dated at 1.3 Ga (e.g., Shih et al. 1999). An age of $2,089 \pm 81 \text{ Ma}$ has been reported for NWA7034 meteorite (Agee et al. 2013). This meteorite is a breccia, and mineral fractions were derived from the bulk sample. Implicit in this age determination is the assumption that all of the breccia fragments and matrix minerals crystallized from the same magma at the same time. Finally a Rb–Sr age of $3.90 \pm 0.04 \text{ Ga}$ was determined on secondary carbonates handpicked from the orthopyroxenite ALH84001 (Borg et al. 1999).

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ values have been determined from the Rb–Sr isochrons and demonstrate a huge range from ~0.701 (e.g., Borg et al. 1997) to 0.723 (e.g., Nyquist et al. 1979a). The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, along with initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, indicate that the shergottites are derived from source regions that have elemental abundances that range from incompatible-element depleted to

Table 2 Representative ages and initial Sr isotopic compositions of Martian meteorites

Sample	Rb–Sr age	Initial ⁸⁷ Sr/ ⁸⁶ Sr	Reference
Zagami (E)	171 ± 8 Ma	0.721566 ± 0.000082	Shih et al. (1982)
EET79001B (I)	172 ± 18 Ma	0.71217 ± 0.00003	Nyquist et al. (1986)
ALH77005 (I)	187 ± 12 Ma	0.71037 ± 0.00005	Shih et al. (1982)
QUE94201 (D)	327 ± 12 Ma	0.701298 ± 0.000014	Borg et al. (1997)
Nakhla	1.30 ± 0.02 Ga	0.70232 ± 0.00006	Papanastassiou and Wasserburg (1974)
Chassigny	1.22 ± 0.01 Ga	0.70253 ± 0.00004	Nakamura et al. (1982)

Letters after shergottite names refer to incompatible-element characteristics of their source regions (E) = enriched, (D) = depleted, and (I) = intermediate

incompatible-element enriched. The shergottites have consequently been subdivided on this basis (Symes et al. 2008). A sampling of Rb–Sr ages determined for the various types of Martian meteorites is presented in Table 2, with an emphasis on the first age determinations for each meteorite.

Lunar Meteorites

Several relatively young ages have also been determined for lunar meteorites. For the most part, however, Rb–Sr ages have been confined to basaltic samples. Like highland rocks returned by the Apollo missions, the Rb–Sr isotopic systematics of highland clasts present in brecciated meteorites appear to be disturbed by metamorphic processes associated with impact. A good example of such disturbance is in anorthositic meteorite Y86032 that yields a Rb–Sr age of 4.62 ± 0.89 Ga (Nyquist et al. 2006). Metamorphism appears to result in the mobilization, and loss, of Rb from the mafic mineral fractions. Thus, Rb–Sr isochrons are generally disturbed to the older side of the age spectrum.

A few basaltic lunar meteorites have been dated using the Rb–Sr chronometer. An age of $2,990 \pm 18$ Ma was reported for the incompatible-element-enriched LaPaz 02205 meteorite (Rankenburg et al. 2006), whereas low Ti-basaltic meteorites NWA 032 and NWA 4734 yielded ages of $2,947 \pm 16$ Ma (Borg et al. 2009) and $3,083 \pm 42$ Ma (Elardo et al. 2014), respectively. Many of the lunar meteorites were found in desert environments and consequently have Rb–Sr systematics that have been disturbed by terrestrial weathering. The Rb–Sr systematics of NWA4734, for example, is based on a two-point tie line. Luckily this age was confirmed by a more robust Sm–Nd isochron that was derived from additional mineral fractions. Ages determined on lunar basaltic meteorites demonstrate that these samples have crystallization ages that are younger than any samples returned by the Apollo and Luna missions. In fact, the meteorites are the youngest lunar samples known (Borg et al. 2004). This is consistent with the hypothesis that they are derived from different localities on the Moon.

Sm–Nd Chronology of Meteorites

Introduction

Samarium-neodymium ages of meteorites are derived from two independent parent-daughter isotope pairs. The first decay reaction is $^{147}_{62}\text{Sm} \rightarrow ^{143}_{60}\text{Nd} + \alpha + \text{Q}$. The parent isotope ^{147}Sm has a well-defined half-life of 106 billion years corresponding to a ^{147}Sm decay constant of $6.54 \times 10^{-12} \text{ year}^{-1}$. Like the ^{87}Rb – ^{87}Sr decay system (see entry “► [Rb–Sr Dating](#)”), this system is based on the isochron method in which separated mineral fractions of an individual samples are analyzed for $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ and plotted on an isochron diagram (Dickin 2005; Faure 1998; see entry “► [Sm–Nd Dating](#)”). Ages determined from this method are only valid if the aliquots that define the isochron

regression were in isotopic equilibrium. It should be noted that different laboratories have used different Nd isotopic ratios, including $^{142}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{144}\text{Nd}$, and $^{148}\text{Nd}/^{144}\text{Nd}$, as well as different isotopic compositions, to correct for instrument mass fractionation. Caution must therefore be taken when comparing the initial $^{143}\text{Nd}/^{144}\text{Nd}$ values reported from different laboratories.

The second decay reaction is $^{146}_{62}\text{Sm} \rightarrow ^{142}_{60}\text{Nd} + \alpha + \text{Q}$. The parent isotope, ^{146}Sm , is extinct so this system can only be used to date samples older than ~ 4.3 Ga. As a consequence, this system is used almost exclusively to date meteorite samples. Model ages are obtained by determining the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of the sample at the time it formed from the slope of a $^{144}\text{Sm}/^{144}\text{Nd}$ – $^{142}\text{Nd}/^{144}\text{Nd}$ isochron plot. A model age is defined by the time required to produce the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of the sample starting from the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio Solar System at 4,567 Ma. In turn, the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of the Solar System is calculated from the initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio measured on a reference sample of known age. The reference samples used to determine ^{146}Sm – ^{142}Nd ages have traditionally been angrite meteorites (e.g., Nyquist et al. 1994), although eucrites (Boyet et al. 2010) and CAIs (Marks et al. 2014) have been proposed more recently. One obstacle to the application of the short-lived Sm–Nd system to date meteorite samples has been defining the appropriate half-life for ^{146}Sm . Values of 68 Ma (Kinoshita et al. 2012) and 103 Ma (Friedman et al. 1966; Meissner et al. 1987) have both been used to calculate ^{146}Sm – ^{142}Nd ages. Either half-life appears to reproduce Pb–Pb ages on the oldest samples, because the uncertainties on the ^{146}Sm – ^{142}Nd ages are often larger than the difference in ages calculated using the 68 Ma and 103 Ma half-lives. The 103 Ma half-life appears to better reproduce the Pb–Pb and ^{147}Sm – ^{143}Nd ages of young lunar samples, however (Marks et al. 2014).

The chemical purification procedures developed to separate Sm and Nd from matrix start with the purification of Rb–Sr. As a consequence, most Sm–Nd isochrons obtained today on meteorite samples are accompanied by Rb–Sr data from the same fractions. The simultaneous analysis of Sm–Nd and Rb–Sr has made the interpretation of some ages significantly easier, because concordant Sm–Nd and Rb–Sr ages typically indicate that these chronometers record the timing of igneous crystallization. Co-analysis of Sm–Nd and Rb–Sr has demonstrated that the Sm–Nd system is less easy to disturb by post-crystallization metamorphism and secondary alteration than the Rb–Sr system. Thus, many of the most reliable ages obtained on meteorites are currently derived from the Sm–Nd system.

Primitive Achondrites

Lugmair (1974) first proposed using the ^{147}Sm – ^{143}Nd system as a dating method and demonstrated its feasibility by obtaining an age of 4.56 ± 0.08 Ga on the eucrite Juvinas. This was followed by application of the Sm–Nd system to the angrite Angra dos Reis, yielding an age of 4.55 ± 0.04 Ga (Lugmair and Marti, 1977), as well as to lunar samples (e.g., Lugmair et al. 1976). Early in the development of the Sm–Nd chronometer, evidence for live ^{146}Sm was sought, but the results were equivocal (Notsu and Mabuchi 1973; Lugmair et al. 1975). The first clear evidence for live ^{146}Sm came from analysis of Angra dos Reis by Lugmair and Marti (1977). They reported a 60 ppm difference between phosphate and pyroxene mineral fractions and attributed the difference to radiogenic decay of ^{146}Sm . The ^{146}Sm – ^{142}Nd and ^{147}Sm – ^{143}Nd isotopic systems have been used to date many differentiated achondrite meteorites including angrites, eucrites, mesosiderites, a brachinite, and an alcapulcoite. A forthcoming manuscript by Marks et al. (2014) provides a summary of some of these results.

Table 3 Representative ages and initial Nd isotopic compositions of Martian meteorites

Sample	Sm–Nd age	Initial ϵ_{Nd}	Reference
Zagami (E)	166 ± 12 Ma	-7.23 ± 0.17	Borg et al. (2005)
EET79001B (I)	169 ± 23 Ma	-16.9 ± 1.4	Nyquist et al. (2001b)
ALH77005 (I)	173 ± 6 Ma	$+11.1 \pm 0.2$	Borg et al. (2002)
QUE94201 (D)	327 ± 19 Ma	$+47.6 \pm 1.7$	Borg et al. (1997)
Governador Valadares	1.37 ± 0.02 Ga	$+16.7 \pm 0.4$	Shih et al. (1999)

Letters after shergottite names refer to incompatible-element characteristics of their source regions (E) = enriched, (D) = depleted, and (I) = intermediate

Martian and Lunar Meteorites

The Sm–Nd system has also been applied to the Martian suite of meteorites that includes shergottites (basalts), nakhlites (clinopyroxenites), chassignites (dunites), as well as an orthopyroxenite (ALH84001). Application of the Sm–Nd chronometer to these samples is very difficult because they have very low abundances of Sm and Nd, contain phosphate minerals that host the vast majority of the Sm and Nd in the rock, and often contain copious amounts of impact melt. As a consequence, mineral fractions derived from Martian meteorites have some of the lowest abundances of Nd of any planetary sample. Not surprisingly, initial attempts to date Martian meteorites yielded highly disturbed Sm–Nd isochrons (e.g., Shih et al. 1982) that seemed to confirm the original hypothesis that these meteorites underwent extensive metamorphism. Thus, young Rb–Sr and U–Th–Pb ages determined from these meteorites were interpreted to record the timing of this event (Papanastassiou and Wasserburg 1974; Nyquist et al. 1979a, b; Chen and Wasserburg 1986). However, Borg et al. (1997) obtained high purity mineral fractions from QUE94201 that were devoid of impact melt glass that yielded young concordant Rb–Sr and Sm–Nd ages of ~330 Ma and suggested that the young ages recorded the crystallization of the sample. Concordant ages for numerous Martian meteorites have now been obtained using Rb–Sr, Sm–Nd, U–Pb, and Lu–Hf chronometers that support this contention. Although most researchers consider these ages to record igneous crystallization, some still support the older hypothesis that the young ages reflect secondary resetting of the isotopic systems by metamorphism (e.g., Bouvier et al. 2009).

Summaries of Sm–Nd ages for Martian meteorites can be found in Nyquist et al. (2001a) and Borg and Drake (2005). Like the Rb–Sr system, the Sm–Nd system can be used to define 4 general age groups for the shergottites of ~170 Ma, ~330 Ma, ~475 Ma, and ~575 Ma. In addition, the initial ϵ_{Nd} values (see entry “► [Samarium–Neodymium, Model Ages](#)”) determined from the Sm–Nd isochrons demonstrate a huge range from -7 to $+48$ (e.g., Borg et al. 1997, 2005). The initial ϵ_{Nd} values, along with initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, indicate that the shergottites are derived from source regions that have elemental abundances that range from incompatible-element depleted to incompatible-element enriched. Samarium–neodymium ages of ~1.3 Ga have been determined from the nakhlites (e.g., Shih et al. 1999), and ages ranging from 4.0 to 4.5 Ga have been obtained for ALH84001 (Nyquist et al. 1995a; Lapen et al. 2010). A sampling of Sm–Nd ages determined for the various types of Martian meteorites is presented in Table 3. In contrast to the Rb–Sr ages presented in the Rb–Sr chronology of meteorites (see entry “► [Rb–Sr Chronology of Meteorites](#)”), this table emphasizes the more recent chronology for each meteorite because the newer data is generally less disturbed.

Several lunar meteorites have been dated using the Sm–Nd system. Unlike many Apollo samples, the Sm–Nd isotopic systematics of most meteorites appear to be minimally affected by the capture of thermal and epithermal neutrons that are produced in the lunar subsurface by bombardment of

galactic cosmic rays. The oldest sample is an anorthositic clast from Y86032 which yields an age of 4.43 ± 0.03 Ga (Nyquist et al. 2006), making it one of the oldest dated rocks from the Moon. Most other Sm–Nd chronometry has been applied to lunar basaltic meteorites. Samarium-neodymium ages of $2,931 \pm 92$ Ma, $2,993 \pm 32$, $3,106 \pm 44$ Ma, and $2,922 \pm 85$ Ma have been determined for NWA032, NWA773 NWA 4734, and LAP02205 (Borg et al. 2004, 2009; Elardo et al. 2014; Rankenburg et al. 2006) that are in good agreement with Rb–Sr ages determined on the same samples. This suite of basalts is the youngest group of lunar rocks that have been dated from the Moon so far and serves to demonstrate that there is significantly more geologic variation on the Moon than is represented in the Apollo (or Luna) sample collections.

Finally, the age of differentiation of both Moon and Mars has been estimated from Sm–Nd whole rock isochrons completed on lunar samples, including meteorites, and Martian meteorites. The age of lunar differentiation is determined using the Sm/Nd ratio estimated for basalt magma sources from measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured for the whole rocks. The model age is calculated from the slope of a line regressed through whole rock data on a ^{146}Sm – ^{142}Nd isochron plot. The basis of these model ages is the assumption that isotopic variation observed in the basalt source regions reflects fractionation of Sm from Nd associated with solidification of the lunar magma ocean. Ages of $4,329^{+40}_{-56}$ Ma (Nyquist et al. 1995a), $4,352^{+21}_{-23}$ Ma (Rankenburg et al. 2006), $4,313^{+25}_{-30}$ (Boyett and Carlson 2007), $4,340^{+20}_{-24}$ (Brandon et al. 2009), and $4,355^{+31}_{-39}$ Ma (Gaffney and Borg 2014) have been determined by these studies. All ages are within uncertainty of the original model age obtained by Nyquist et al. (1995a) and yield a weighted average age of $4,341 \pm 21$ Ma.

The model age of Martian differentiation has been estimated using the slope of shergottite whole rock $^{142}\text{Nd}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic data to be $4,513^{+27}_{-33}$ Ma (Borg et al. 2003), $4,525^{+19}_{-21}$ Ma (Foley et al. 2005), and $4,502 \pm 5$ Ma (Symes et al. 2014). It has also been determined from ^{146}Sm – ^{142}Nd whole rock isochron to be $4,527 \pm 18$ Ma (Caro et al. 2008) and from model age determined on individual samples to be $4,535 \pm 7$ Ma (Debaille et al. 2007). All ages are within uncertainty of the original model age determined on QUE94201 of $4,525 \pm \sim 25$ Ma (Borg et al. 1997). The weighted average of all these ages is $4,505 \pm 11$ Ma, indicating that the Moon differentiated significantly after Mars.

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Seawater Sr Curve

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Definition

The seawater Sr curve is a proxy record of the $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater through time, as reconstructed from well-preserved minerals precipitated from seawater.

Introduction

Prior to the development of the analytical technique to measure precise strontium isotope ratios, Wickman (1948) predicted that the ratio of radiogenic to unradiogenic strontium ($^{87}\text{Sr}/^{86}\text{Sr}$), as measured in carbonates and evaporate minerals precipitated from seawater, might be used as a tool to date ancient marine sediments. Wickman's rationale was straightforward, even if, upon hindsight, partially incorrect and incomplete: the gradual concentration of Rb in the continental crust and decay of radiogenic ^{87}Rb would result in monotonically increasing $^{87}\text{Sr}/^{86}\text{Sr}$ values of the crust and hence a steady rise in seawater strontium isotope composition over geological time. He presciently noted that due to the effective separation of Sr and Rb in carbonates, in particular mollusk shells, limestone was the ideal target for determining ancient seawater Sr isotope ratios. Although $^{87}\text{Sr}/^{86}\text{Sr}$ is now measured on a wide variety of minerals, well-preserved foraminifera tests and brachiopod shells are among the prime targets for Sr isotope chemostratigraphy of Phanerozoic sediments (Veizer et al. 1999; McArthur et al. 2012).

Burke et al. (1982) published the first comprehensive record of Phanerozoic $^{87}\text{Sr}/^{86}\text{Sr}$, which revealed multiple peaks and troughs that correspond in part to major plate tectonic events. This entry firmly established the application of strontium isotope chemostratigraphy as a geochronological tool with wide applications in Earth history. The history of the development of the seawater Sr curve and the fundamentals of its application are briefly reviewed here. For a thorough treatment of strontium isotope stratigraphy and its geochronological applications, the reader is referred to the recent review by McArthur et al. (2012).

Development and Application of the Method

With the development of techniques to separate strontium and analyze its isotopic ratios by solid source mass spectrometry, Wickman's (1948) hypothesis that seawater $^{87}\text{Sr}/^{86}\text{Sr}$ changed through time was put to the test in the 1950s and 1960s. Early results suggested that due to a combination of lower-than-predicted variation in Rb/Sr ratios in rock-forming minerals, poor age control on samples, and as yet limited analytical precision, strontium isotopes might not live up to their

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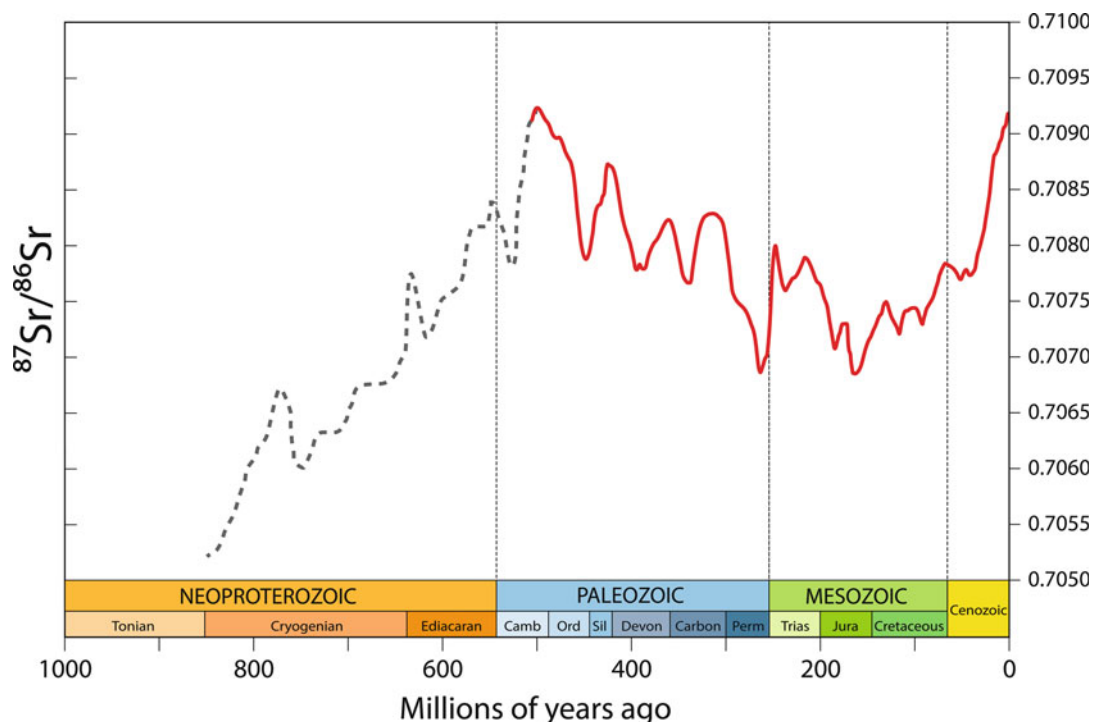


Fig. 1 The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the past 1.0 billion years. The Ordovician–Present portion of the curve is the LOWESS fit from McArthur et al. (2012), updated from McArthur et al. (2001). The Neoproterozoic–Cambrian portion of the curve (*dashed line*) is much more poorly calibrated and of lower resolution (Adapted from Shields and Veizer (2002) and Halverson et al. (2007, 2010))

promise as an effective tool in dating ancient marine sediments (Gast 1955). However, geochemists did not give up, and subsequent application of the technique highlighted the potential to unravel past geological processes, including growth of the continental crust, using the strontium isotope system (e.g., Hurley et al. 1962; Hedge and Walthall 1963).

Another early target of the Sr isotope method was in characterization of seawater (e.g., Compston and Pidgeon 1962; Hedge and Walthall 1963; Faure et al. 1965). This work demonstrated that the strontium isotope composition of the present oceans is effectively uniform (0.7092) due to the long residence time of strontium in the oceans ($\sim 3\text{--}5 \times 10^6$ years) versus the effective mixing time of the oceans ($\sim 10^3$ years). Faure et al. (1965) further argued that seawater composition at any given time was the result of a mixture of Sr from several different reservoirs with strongly contrasting strontium isotope ratios, most notably mafic versus felsic continental crust and marine carbonates. Armstrong (1971) proposed that weathering related to continental glaciation might also exert a strong influence on seawater Sr isotope compositions.

Hedge and Walthall (1963) published the first dataset on ancient carbonates and argued that these limited data supported a roughly linear evolution in marine $^{87}\text{Sr}/^{86}\text{Sr}$ over geological time, consistent with Wickman's (1948) hypothesis. However, Peterman et al. (1970) published the first Phanerozoic seawater strontium isotope curve, which, although at a low resolution (by modern standards) and limited by poor age constraints, showed that $^{87}\text{Sr}/^{86}\text{Sr}$ both rose and decreased during the Phanerozoic, with a notable trough across the Jurassic–Cretaceous boundary. Veizer and Compston (1974) subsequently upgraded the Phanerozoic record, taking into account diagenetic effects on $^{87}\text{Sr}/^{86}\text{Sr}$ in marine carbonates and applying the now canonical principle that the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values for rocks of any given time interval most reliably record coeval seawater

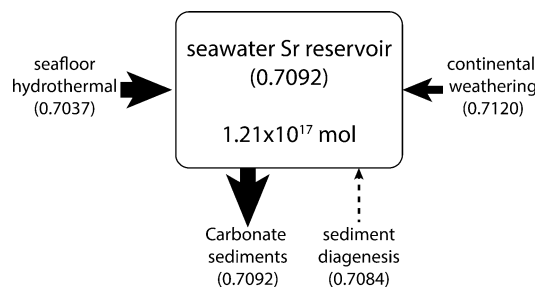


Fig. 2 A basic box model illustrating the marine Sr cycle with present strontium isotope compositions for fluxes and reservoirs. The main sources of seawater Sr are the seafloor hydrothermal flux and the continental weathering flux. The sizes of the arrows scale to the relative size of the associated flux into and out of the ocean (from Banner 2004). Note that the flux from diagenesis of marine sediments (dominated by carbonates) is effectively negligible because it releases strontium with nearly the same composition as the seawater reservoir (Kump 1989). Strontium is removed from seawater as a trace component of marine carbonates (and to a minor extent sulfates)

composition. This compilation confirmed the late Jurassic–Cretaceous $^{87}\text{Sr}/^{86}\text{Sr}$ trough and also revealed a prominent Cenozoic rise in $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 1).

A decade later, Burke et al. (1982) published a much higher-resolution Phanerozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$ compilation that reproduced the broad patterns documented by Veizer and Compston (1974) but also demonstrated a more complex history of seawater strontium, with multiple peaks, troughs, and intervals of rapid change. Burke et al. (1982) interpreted the fluctuations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in terms of the competing influence of unradiogenic (~ 0.7035) strontium derived from mid-ocean ridges (i.e., hydrothermal) and radiogenic strontium (~ 0.720 at present) derived from weathering of the continents (Fig. 2), with carbonate-derived (weathered) strontium acting as a buffer rather than a driver of change. These fluctuations, they argued, corresponded to tectonic events and reorganization of the continents during the Phanerozoic. This compilation also implicitly demonstrated a much improved potential for using strontium isotopes in marine carbonates as a dating tool, in particular during intervals of rapidly evolving $^{87}\text{Sr}/^{86}\text{Sr}$, such as the Cambro-Ordovician, Permian, and Jurassic (McArthur et al. 2001). DePaolo and Ingram (1985) later showed how high-precision Sr isotope chemostratigraphy could be used as a more effective dating tool than paleomagnetism and stable isotope chemostratigraphy during intervals such as the past 35 m.y., where $^{87}\text{Sr}/^{86}\text{Sr}$ has been rising steadily and rapidly, presumably due in large part to the Alpine–Himalayan orogeny (Edmond 1992) and/or Antarctic glaciation (Zachos et al. 1999).

Subsequent work on the seawater strontium isotope curve has involved focused efforts to produce high-resolution records through specific time intervals (e.g., De Paolo and Embry; Koepnick et al. 1990; Paytan et al. 1993; Shields et al. 2003), comprehensive Phanerozoic compilations from well-constrained and well-preserved samples (McArthur 1994; Veizer et al. 1999), and Precambrian compilations (Shields and Veizer 2002), most specifically for the Neoproterozoic (1,000–541 Ma), which shows changes comparable to the Phanerozoic (Shields 2007; Halverson et al. 2007; Fig. 1). Strontium isotope chemostratigraphy has proven particularly valuable in the Neoproterozoic, where lack of biostratigraphic constraints and consequent poor age control necessitate alternative dating methods.

Sample Selection and Diagenetic Considerations

As Wickman (1948) noted, the best materials for strontium isotope chemostratigraphy are minerals that precipitated from seawater. Many different materials have been explored and analyzed as proxies for seawater composition, including both aragonite and calcite bulk rock, shells, otoliths (fish ear bones), other biogenic and inorganic CaCO_3 precipitates, phosphatic material such as conodonts, and sulfates, namely, evaporite minerals (e.g., CaSO_4) and barite (BaSO_4). Due to the relatively high Sr concentration in primary aragonite (up to 1 wt%), originally aragonitic tests and shells (and to a lesser extent early marine cements) may be good targets for Sr isotope analyses. However, primary aragonite is unstable in the diagenetic realm and rare in the geological record. Furthermore, the type of materials available for strontium isotope stratigraphy is heavily dependent on geological age. Calcitic foraminifera tests recovered from deep sea cores have proven to be well suited for the Cenozoic record (McArthur et al. 2012), whereas brachiopod shells (Veizer et al. 1999) and belemnite guards (Jones et al. 1994) are among the most robust proxies for the Mesozoic and Paleozoic eras.

The paucity to absence of biogenic carbonates in Cambrian and older strata necessitates the use of bulk rocks for strontium isotope analyses. Conveniently, seawater and calcite contain only trace amounts of Rb; unfortunately, carbonate sediments also typically contain an acid insoluble (detrital) component, resulting in a degree of ingrowth of ^{87}Sr from detrital ^{87}Rb , mostly from clays. Coupled with loss of Sr during diagenesis, this can result in significantly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values in the carbonate fraction, even in carefully processed carbonate samples. Techniques are available for correcting for radiogenic ^{87}Sr ingrowth (e.g., McArthur 1994); however, where possible, low-Rb carbonates should be targeted for Sr isotope stratigraphy. Analyzing multiple samples from the same or closely spaced stratigraphic horizons is also useful in determining the pattern of alteration of $^{87}\text{Sr}/^{86}\text{Sr}$ during diagenesis (Banner and Hanson 1990; McArthur et al. 2012) and constraining the most likely seawater composition, which is typically assumed to be less than or equal to the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ value.

The crystal lattice of dolomite, a common secondary carbonate mineral, does not accommodate the relatively large Sr^{2+} cation. Hence, dolostones, which comprise a significant fraction of the stratigraphic record, have sparingly low Sr concentrations (typically less than 100 ppm), making them highly prone to isotopic overprinting and in most cases unsuitable for strontium isotope stratigraphy. Other carbonate minerals, such as ankerite and siderite, typically form authigenically and hence are also poor proxies for seawater Sr isotope composite.

Analytical Techniques

Sample preparation and analyses for Sr isotopes on carbonate minerals (and other seawater precipitates) involve four steps: sample selection, sample cleaning and dissolution, chemical separation, and measurement of isotope ratios by mass spectrometry. Because only samples with minimal Rb contents consistently yield reliable data, only Sr isotope ratios (and not precise Sr or Rb concentrations) are typically measured for Sr isotope stratigraphy, hence eliminating the requirement to add an isotopic tracer solution, unless a radiogenic ingrowth correction is required:

1. Sample selection is performed based on a combination of petrographic and geochemical prescreening. Those samples showing the least recrystallization and overprinting by secondary

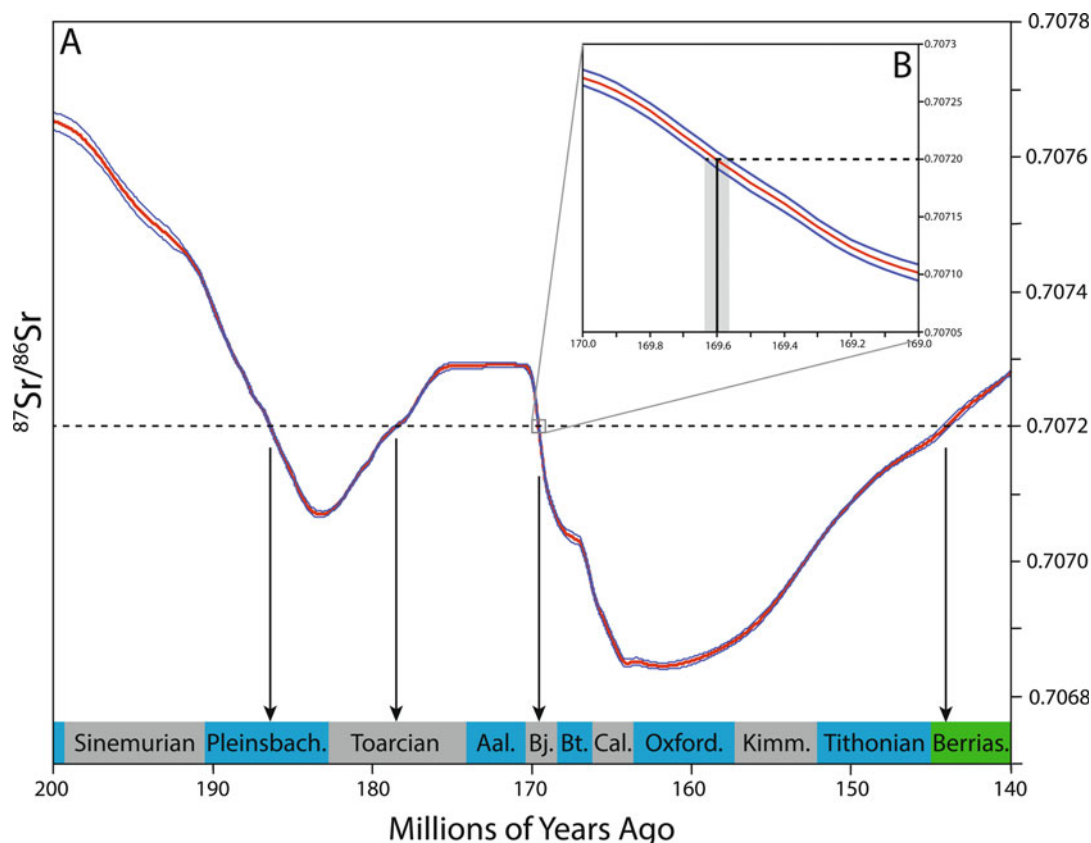


Fig. 3 A. The LOWESS fit Sr isotope curve for the time interval 200–140 Ma ago (Jurassic stages in *blue* and *gray*: *Aal* Aalenian, *Bj* Bajocian, *Bt* Bathonian, *Cal* Callovian, *Kimm* Kimmeridgian. Cretaceous Berriasian stage is in *green*), from McArthur et al. (2012). The *red* line is the LOWESS fit, and the *blue* lines mark the upper and lower 95 % confidence intervals. *Dashed* line at $^{87}\text{Sr}/^{86}\text{Sr} = 0.70720$ demonstrates the nonuniqueness of this value during the Jurassic, where it occurs during four distinct stages. B. Inset is a zoom-in of the interval from 170 to 169 Ma. If a sample with a Sr isotope composition of 0.70720 is known to be Bajocian in age (e.g., based on biostratigraphy or other chemostratigraphic data), then an age can be determined by comparison with the reference curve. In this case, a value of 0.70720 yields an age of $169.60 \pm \sim 0.04$ Ma (note that the error does not factor in uncertainty related to the calibration of the time scale)

cements, relatively high Sr/Rb ratios (or in the absence of Rb data, high Sr/Ca ratios), and low detrital component are best suited for Sr isotope analyses.

2. Sample dissolution is usually performed in a dilute acid such as weak acetic acid, which minimizes partial dissolution of the non-carbonate fraction. In order to further reduce incorporation of detrital strontium, it is common to pre-leach sample powders in ammonium acetate, which removes loosely bound Sr ions (Bailey et al. 2000). A prewash with methanol (McArthur et al. 2006) is also effective in removing clays from a sample powder, reducing the potential for leaching of detrital strontium during sample dissolution.
3. Dissolved samples are passed through an ion exchange resin (e.g., Eichrom™ Sr-spec resin) to separate Sr from other ions (see also entry on ► [Chromatography](#)), most importantly Ca and Rb, which can greatly affect Sr isotope measurements.
4. Traditionally, Sr isotope analyses have been performed by solid source, thermal ionization mass spectrometry (TIMS; see also entry on ► [Mass Spectrometry](#)). Measured $^{87}\text{Sr}/^{86}\text{Sr}$ values are corrected against an international standard, usually NIST (NBS) 987, with an accepted $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.710248. Reproducibility is commonly as good as ± 0.000005 (2σ). Strontium isotope

ratios may also be measured in solution or by laser ablation on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). These techniques are faster, and laser ablation has the advantage that it does not require time-consuming chemical separation. However, they also yield less precise results than TIMS, although reproducibility as low as ± 0.00001 (2σ) has been achieved in solution mode (e.g., Balcaen et al. 2005). Similar precision and accuracy has not yet been realized by laser ablation MC-ICP-MS, but the technique is increasingly applied to high spatial resolution analyses of media such as fish otoliths, bones, and teeth where the high precision provided by TIMS analysis is not required (Copeland et al. 2010).

The Strontium Isotope Seawater Curve (1.0–0 Billion Years)

Since Burke et al. (1982) published their record of Phanerozoic seawater $^{87}\text{Sr}/^{86}\text{Sr}$, a great deal of work has gone both into developing high-resolution records for specific intervals of the Phanerozoic (e.g., Koepnick et al. 1990; Fig. 3) and in producing compilations of the highest-quality and best dated samples (Veizer et al. 1999; McArthur et al. 2001). The most comprehensive compilation of Phanerozoic $^{87}\text{Sr}/^{86}\text{Sr}$ data is found in the database of McArthur et al. (2001), which has been progressively updated (e.g., McArthur and Howarth 2004; McArthur et al. 2012), and now comprises over 4,000 data points from some 50 sources (McArthur et al. 2012). The construction of such a record requires the application of age models to specific data sets, the integration of these data sets, and a technique for fitting a curve to the data, which can then be used to calculate an age and appropriate error (see Howarth and McArthur 1997, for detailed description of data treatment and analysis for the Phanerozoic seawater Sr curve shown in Fig. 1). For the relatively well-dated Phanerozoic record, age models are reasonably robust and there exist high-resolution records, resulting in typical 95 % confidence intervals about the best-fit curve of 0.00001–0.00004 (McArthur et al. 2012).

The most complete database for Precambrian strontium isotopes is from Shields and Veizer (2002). However, the age constraints on Precambrian samples are deficient, and the quality of data is lower and more difficult to verify than for the Phanerozoic. Here, we include only data from 1.0 billion years onward because the pre-1.0 Ga record is poor and shows only limited change, in contrast with the 1,000–485 Ma Sr isotope record, which has been extensively studied and shows significant variability. Because the resolution and quality of the data from this time interval is low, rigorous fitting techniques as used for the Phanerozoic record are not yet applicable.

The Proterozoic–Phanerozoic strontium isotope seawater curve (Fig. 1) reveals many striking features. The first-order trend is one of increasing $^{87}\text{Sr}/^{86}\text{Sr}$, which results from the progressive decay of ^{87}Rb (Wickman 1948; Shields 2007). The second-order pattern is one of peaks at present and c. 500 Ma ago and troughs at about 180 and 1,000 Ma ago, which may reflect the cycle of supercontinental breakup and assembly (Halverson et al. 2007). Superimposed on this pattern are prominent fluctuations, some by as much as 0.001, over intervals of a few to 25 Ma, many of which closely correspond to tectonic events.

The main parameters controlling the seawater Sr isotope composition are the magnitude of the seafloor hydrothermal flux (both mid-ocean ridge volcanism and off-axis alteration of the seafloor) and continental weathering and their respective $^{87}\text{Sr}/^{86}\text{Sr}$ values. The composition of the seafloor flux (≈ 0.7037 ; Banner 2004) is approximately fixed by mantle composition, whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ of continental weathering is presently ≈ 0.712 (Fig. 2) but presumably varied considerably through time. Because the residence time of Sr in the oceans is ~ 5 Ma and there are no plausible

mechanisms to increase or decrease the flux into or out of the oceans rapidly, changes in $^{87}\text{Sr}/^{86}\text{Sr}$ are steady state (i.e., gradual; see also entry on ► [Marine Isotope Stratigraphy](#)). In principle, changes in any one of the four major influx parameters (Fig. 2) can drive a change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$, but due to the large isotopic difference between the hydrothermal and continental weathering sources, many researchers invoke changes in the relative contribution of these two fluxes to explain changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. On the other hand, although the continental flux is buffered by the weathering of marine carbonates, the huge variations between different rivers (Gaillardet et al. 1999) suggest that the continental weathering flux should have changed substantially through time as a result of paleogeographic evolution of the continents and paleoclimate.

Use as a Geochronological Tool

Given a reference seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve, dating a marine rock or sediment of poorly constrained age may be accomplished by comparing its strontium isotope composition to a reference curve. However, the effectiveness of this tool is contingent upon the age and available age constraints on that sample, whether or not there are strontium isotope data from overlying or overlying strata, and the robustness of the curve. For example, a marine carbonate sample that is known only to be Jurassic or early Cretaceous in age and has an $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.70720 could equally be Pliensbachian (190.8–182.7 Ma), Toarcian (182.7–174.1 Ma), Bajocian (170.3–168.3 Ma), or Berriasian (145.0–139.4 Ma) in age (Fig. 3A). However, if the stage of the sample is known through biostratigraphy or other chronostratigraphic constraints, then the age can be specified more precisely (Fig. 3B), with the precision being a measure of the confidence interval for the Sr isotope curve at that age (Fig. 3) and the uncertainty in the age model upon which the reference Sr isotope curve is constructed (McArthur et al. 2012).

In the absence of additional age constraints that eliminate some of the possible matches between the sample and the reference curve, it helps to match both the absolute value and stratigraphic (i.e., temporal) trends. For example, if multiple samples from different stratigraphic levels are analyzed from the section containing the original sample of interest, then these can be used to determine the trajectory in $^{87}\text{Sr}/^{86}\text{Sr}$. If the samples show a trend of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ up-section (i.e., in progressively younger rocks), then this pattern eliminates either a Toarcian or Berriasian age, both of which correspond to intervals of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 3A). Whereas the slope of the declining trends ($d[^{87}\text{Sr}/^{86}\text{Sr}]/dt$) differs between the Pliensbachian and Bajocian, it would be virtually impossible to use the distinction alone in a poorly dated section of strata to discriminate between these two ages. Rather, a more complete $^{87}\text{Sr}/^{86}\text{Sr}$ profile that captured, for example, the late Pliensbachian trough (0.707075) or the continued decline to $^{87}\text{Sr}/^{86}\text{Sr}$ values lower than 0.707075 in the Bathonian (Fig. 3) would be required. Alternatively, additional chemostratigraphic data such as carbonate carbon isotopes or sulfate sulfur isotopes (see entry on ► [Marine Isotope Stratigraphy](#)) or magnetic polarity data may provide sufficient constraints to narrow down the appropriate age for the 0.70720 sample.

Other Applications

The seawater strontium isotope curve has other useful applications in stratigraphy. By comparing the Sr isotope trend of a given succession of strata to the reference curve, sediment accumulation rates can be reconstructed. This application is most useful where the rate of change in $^{87}\text{Sr}/^{86}\text{Sr}$ is

high and of limited to no use where the rate of change is low or effectively nil (McArthur et al. 2012). Strontium isotopes are also useful for detecting and quantifying breaks in the stratigraphic record. Because seawater Sr isotope composition evolves gradually, any abrupt shifts within strata must record either a depositional hiatus (diastem) or an erosional disconformity. Again, this application works best where the rate of change in $^{87}\text{Sr}/^{86}\text{Sr}$ is high, in which case the offset in $^{87}\text{Sr}/^{86}\text{Sr}$ across a stratigraphic boundary can be used to approximate the amount of time missing at that stratigraphic level.

Summary and Conclusions

Strontium isotope stratigraphy has important applications as a chronostratigraphic tool. The basis for this dating method is the construction of a reference seawater strontium curve against which undated or poorly dated samples can be compared. The ability to date a given sedimentary sample or interval of strata depends on several factors: (1) the reliability of that sample as a proxy for seawater composition and the protocol by which it is analyzed, (2) independent constraints on the approximate age of that sample, and (3) the precision of both the age model and the Sr isotope data upon which the appropriate reference seawater Sr isotope curve has been constructed. A high-precision Sr isotope curve now exists for the interval from the Ordovician through the present (McArthur et al. 2012), and a lower-resolution and as yet poorly age-calibrated record for the Neoproterozoic–Cambrian is available (Fig. 1). The reliability of strontium isotope stratigraphy as a dating tool decreases with increasing age; however, its importance increases with older rocks because other dating methods are rare or less reliable. For example, in the absence of a robust biostratigraphy for Precambrian strata, strontium isotope stratigraphy will play an important role in defining the geological time scale for these older rocks.

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Terrestrial Cosmogenic Nuclide Dating

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Synonyms

Burial dating; Cosmic ray exposure (CRE) dating; Cosmogenic nuclide isochron dating; Cosmogenic radionuclide (CRN) dating; Depth profile dating; Surface exposure dating (SED); Terrestrial in situ cosmogenic nuclide (TCN) exposure histories

Definitions

Cosmic rays are high-energy (10^4 to 10^{20} eV) particles composed mostly (90 %) of atomic nuclei but with some photons (gamma rays), electrons, and positrons. The majority (90 %) of the atomic nuclei are protons (H nuclei), the rest are alpha particles (He nuclei, 9 %) and nuclei heavier atoms (1 %). Two major sources of this **primary cosmic radiation** are the Sun whose flux peaks at ~100 MeV (solar cosmic rays, **SCR**) and our galaxy, the Milky Way, with the flux peak between 300 MeV and 1 GeV (galactic cosmic rays, **GCR**). We believe GCR is produced primarily in supernova events (an inference suggested by the excess over cosmic abundance of heavy nuclei).

Secondary cosmic radiation (or “secondaries”) refers to the cascade of particles produced by the interaction of primary cosmic rays with the atmosphere and the surface of the Earth. Because of the high energies of the incoming particles, a wide spectrum of hadrons, mesons, and leptons are produced. The lifetimes of many of these secondary particles are so short that they decay in a shower of lighter particles before they can interact with another atom of the material through which they are passing, but others do interact, producing yet another cascade. Ultimately, the flux is dominated by the longer-lived particles and by the particles with small interaction cross sections. By the time the primaries have passed through 10 % of the atmosphere, the secondary flux is predominately pions, kaons, protons, neutrons, muons, electrons, positrons, and gamma rays (photons). These secondaries will produce larger nuclei (cosmogenic nuclides) in the atmosphere and minerals.

Cosmogenic nuclides are produced through any interaction of primary or secondary cosmic radiation with matter. While some notable cosmogenic nuclides (isotopes) are produced from SCR (e.g., atmospheric radiocarbon is produced from low-energy (thermal) *neutron capture* by nitrogen: $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$), the majority of TCN production is through *spallation* of a target nucleus which requires GCR primaries or secondaries with sufficient energy to exceed the binding energy of the target nucleus (a minimum of >3 MeV per target nucleon). Cosmogenic nuclides need to be distinguished from radiogenic and nucleogenic nuclides. A **radiogenic nuclide** is a daughter product of a radioactive decay (fission, beta, alpha). For U-dating methods or (U–Th)/He thermochronology, ^{234}Th + ^4He are radiogenic products of the α -decay of ^{238}U . A **nucleogenic**

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nuclide is produced when an energetic radiogenic particle interacts with another nucleus just after decay of its parent. For example, ^{10}Be can be produced in a lithium-rich mineral via $^7\text{Li}(\alpha, p)^{10}\text{Be}$.

Cosmogenic nuclide dating uses the accumulation, production, or decay of cosmogenic nuclides to determine the exposure history of near-surface samples (top tens of meters on Earth or top hundreds of meters in space). This can be accomplished by measuring a cosmogenic isotope that has been produced in situ in a mineral on a rock surface or that has been produced in the atmosphere and subsequently accumulated in a soil. For instance, the concentration of ^{10}Be accumulated in a saprolite will depend on the flux of ^{10}Be in precipitation and dust delivered to the soil, the abundance and type of clay that holds the ^{10}Be , and the duration that the soil is at the surface. In addition to exposure ages, the method can determine whether a sample was at the surface or beneath it, whether the sample's position was stable or eroding, and whether the sample's surface history was interrupted by periods of burial. Examples of applications of cosmogenic nuclides that are produced in situ, but not in Earth's lithosphere, include surface exposure dating on Martian (Farley et al. 2014) and lunar surfaces (Drozd et al. 1974) and the size and exposure history of meteorites (Eugster et al. 2006). Cosmogenic nuclides produced in the atmosphere include ^{14}C (thermal-neutron capture by N). Radiocarbon dating has been widely applied for dating objects of importance in defining geologic and archaeologic chronologies; in testing the authenticity of objects of art, or worship, or historic significance; and, on even shorter time scales, in studying the inception and progress of disease in a living organism. ^{14}C has been used to study atmospheric mixing, verify the global circulation model of the oceans, and follow the fate of anthropogenic carbon in the biosphere and oceans. ^{36}Cl produced in the atmosphere by cosmic ray-induced spallation of argon has been used primarily by hydrologists to study the recharge histories of hydrologic systems. ^{10}Be and ^7Be produced in the atmosphere have been used to estimate ages of soils and ground ice (e.g., Gilichinsky et al. 2007) or rates of erosion of catchments (Brown et al. 1988) and study the behavior of aerosol deposition and air mass mixing.

Broadly, there are three types of systems that are dated using cosmogenic nuclides: (1) those in which the cosmogenic nuclide is produced in situ in a solid, e.g., ^{10}Be in rock; (2) closed systems in which the in situ production has stopped because of the complete shielding of a sample from cosmic rays, e.g., $^{26}\text{Al}/^{10}\text{Be}$ in deeply buried quartz; and (3) a now-closed system that formerly was in equilibrium with a reservoir that had a constant or known concentration of a cosmogenic nuclide, e.g., ^{14}C in *any* biogenic material; the reservoir is either the atmosphere or ocean.

This entry treats the open system and closed system (1 and 2) applications of nuclides specifically produced in exposed minerals near Earth's surface, to determine an exposure age of a surface, burial duration of minerals, or erosion rate of surfaces and catchments (Lal 1991). The term **terrestrial in situ cosmogenic nuclide (TCN)** exposure history describes this method, which utilizes a growing knowledge of how production rates spatially and temporally vary on Earth owing to variations in the geomagnetic field and atmospheric shielding. TCN methods are distinguished from methods using meteoric cosmogenic nuclides, even when the latter are absorbed by clays in soil and marine sediments or accumulated in various water reservoirs (e.g., ice sheets, groundwater). The term **CRN** excludes the stable cosmogenic nuclides (e.g., ^3He , ^{21}Ne , ^{38}Ar), **SED** can be achieved with other dating methods (e.g., luminescence), and **CRE** dating can be conducted on lunar and other planetary surfaces.

The TCN dating method is a *numerical dating method*. Currently the TCN production rates have been calibrated against other dating methods owing to the difficulty of obtaining precise cross sections for the production of each isotope through different interaction pathways. This would suggest that it is calibrated, such as lichenometry or the geomagnetic secular variation dating method. However, with improvements in our understanding of the temporal and spatial variations

in the geomagnetic field, cosmic ray interactions, nuclear cross sections, production rates, and depth profile shapes are becoming reliably predicted by theory (Masarik and Reedy 1995; Argento et al. 2013). In this sense, the TCN dating method is a numerical, *not calibrated*, method. The TCN method is distinct from cosmogenic dating methods based on correlation. For instance, meteoric cosmogenic nuclides measured in time series media – such as ^{10}Be in glacier ice (Beer et al. 1987) or marine sediment (Morris et al. 2002) – can provide a reliable method for correlating undated records to meteoric cosmogenic nuclide records in independently dated cores.

Introduction

TCN exposure methods are used to determine the duration of exposure to cosmic rays, duration and degree of shielding from cosmic rays, and rate and style of erosion, on or near Earth's surface. The premise is that the measured concentration of TCN is proportional to the duration that the mineral has been exposed to cosmic rays (Fig. 1) and, in the case of a radioactive TCN in a shielded sample, how much time the concentration has decayed.

Depending on the energy and type of incident cosmic ray particle and target nucleus, cosmic ray interactions produce a variety of secondary particles over a wide energy spectrum, including gammas, electrons, kaons, pions, muons, neutrons, protons, deuterons, tritons, ^3He nuclei, alphas, and heavier nuclides. It is the heavier nuclides that are of interest. However, to be useful for exposure dating, the TCN should:

- Be stable or have suitably slow decay rates
- Be more abundant than the radiogenic or nucleogenic species in the target mineral
- Have in situ production rates that yield extractable concentrations that can be resolved against its elemental isotopes
- Be precisely measurable considering blanks, detection limits, and isobaric interferences

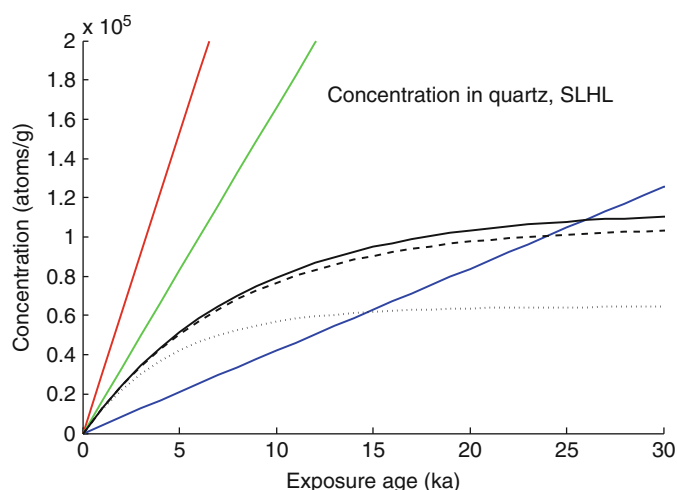


Fig. 1 Gradual buildup of four TCNs in quartz at sea level high latitude. Black, ^{14}C ; green, ^{21}Ne ; blue, ^{10}Be ; and red, ^{26}Al . Continuous production by spallation only, with rates according to Borchers et al. (submitted) and Kober et al. (2011). Solid lines represent surfaces with zero erosion. Constant continuous erosion of 5 and 10 mm ka^{-1} shown with dashed and dotted curve for ^{14}C

- Be produced in stable, chemically resistant minerals that are common and have low thermal diffusivities for noble gases at surface temperatures

This greatly reduces the number of useful particles, and currently only 6 TCNs are widely used: ^3He , ^{10}Be , ^{14}C , ^{21}Ne , ^{26}Al , and ^{36}Cl (Table 1). The probability for cosmic ray interaction – cross section, measured in barns – takes into account the type and energy of the incident secondary and target nuclei. Thus, each TCN is produced at a unique rate, depending on the energy of the cosmic radiation, the type of interactions of which there are five (spallation, thermal and epithermal neutrons, and interactions of negative and fast muons), and the chemistry of the mineral. Although quartz is the most commonly used mineral, other minerals include calcite, feldspar, garnet, hornblende, magnetite, olivine, pyroxene, and sylvite. With the general exception of quartz, the chemical composition of each mineral should be measured to determine the abundance of suitable target nuclei for each of the five interactions. Quartz is unique in that its composition is stoichiometric, eliminating the need to analyze its chemical composition to determine the different production rates. For instance, ^{10}Be is produced in quartz from spallation and muonic interaction on Si and O at a rate of about 4 atoms $\text{g}^{-1} \text{year}^{-1}$ at sea level, high latitude, under current atmospheric and magnetic field conditions. Until recently, even whole rock samples have been analyzed for ^{36}Cl , ^{10}Be , and ^{14}C , giving the possibility that any lithology can be used if the TCN production rates for the specific rock composition can be determined. Thus, every TCN-mineral system is a unique clock. Ratios of multiple TCN can be measured in a single mineral (e.g., ^{10}Be , ^{14}C , ^{21}Ne , and ^{26}Al in quartz, Fig. 1) or in the same rock (^{36}Cl in feldspar and ^3He in olivine in basalt).

The TCN exposure methods differ from other dating methods. Both radioactive and stable (noble gas) isotopes can be used. The concentration of the isotopes is generally depth dependent, unlike other radiometric chronometers which are dependent on the parent isotope abundance. The technique is not temperature dependent as is the case for thermochronometry and amino racemization. Unlike most geochronometers, the TCN method is not necessarily restricted to specific minerals with a certain isotopic abundance, although production rates are currently well known for relative few minerals.

Table 1 Commonly used terrestrial cosmogenic nuclides

Nuclide	ET	ATM	Half-life (ka)	Isotope	Isobar	TCN analysis	TCN production mechanisms	Target minerals
^3He	•		Stable	^4He	^3H	NGMS	nf	Ol
^{10}Be	•	•	1,390	^9Be	^{10}B	AMS	nf, μ	Qtz
^{14}C		•	5.73	$^{12/13}\text{C}$	^{14}C	AMS	nf, μ , nt	Qtz
^{21}Ne	•		Stable	$^{20/22}\text{Ne}$		NGMS	nf, μ	Qtz
^{26}Al	•	•	720	^{27}Al	^{26}Mg	AMS	nf, μ	Qtz
^{36}Cl	•	•	300	$^{35/37}\text{Cl}$	^{36}S	AMS	nf, nt, μ	K, Ca-rich

Notes

Cosmogenic $^{37-38}\text{Ar}$ is not listed as it is not widely used as a TCN owing to difficulties in isolating it from the radiogenic components

ET, ATM: these nuclides are also measured in extraterrestrial and atmospheric/meteoritic targets

Isobar: listed are the most important isobaric interferences; recent isobaric separation innovations have greatly reduced the impact of isobars on low-level TCN measurements

Production pathways: nf, spallation by fast neutrons; nt, thermal (and epithermal) neutron capture; μ , fast and negative muonic interactions

Target minerals: only the most commonly utilized minerals are listed. For ^{36}Cl and $^{37-38}\text{Ar}$ feldspar separates are now used more than whole rock

Examples of TCN Exposure and Burial Dating

Details of the measurement and interpretation of TCN are provided below. Table 2 provides an indication of the wide range of applications of the method. Currently the most widely used application of TCN methods is exposure dating of glacial boulders for moraine chronologies, followed by the application of TCN to provide age control on alluvial strain markers for fault kinematics, and catchment average erosion rates.

Range of Applicability

The applicable range for TCN dating crosses seven orders of magnitude – more than any other dating method. Theoretically, the lower limit of the surface exposure dating method is $\sim 10^0$ years. While exposure ages of years have been determined, the technique is practically limited by the difficulty of measuring low concentrations (i.e., few hundreds of atoms per gram of mineral, requiring a large

Table 2 Examples of applications of TCN methods

Method	Landform/material	Purpose/test
Exposure dating	Lava surface	Eruption age or recurrence rate
	Bedrock fault scarp	Variation in slip rate with time
	Landslide scarp face	Acceleration of mass movement
	Erratics on moraine, esker, or plain	Timing of deglaciation, retreat rate
	Boulders on alluvial fan	Age of strain markers for fault kinematics
	Boulders on a beach	Isostatic uplift rate or tilt rate of raised shorelines
	Impact ejecta	Age of impact
	Bedrock mountain peaks, tors	Age of formation, timing of last glaciation
	Precariously perched boulders	Timing of seismicity for a given acceleration
	Overturned boulders	Timing of last major flood event
	Colluvial blocks	Timing of last seismic shaking
	Submarine cobble on continental shelf	Duration of shelf exposure
	Debitage, quarried tools	Timing of human occupation
Depth profile dating	Multiple sand samples in a terrace	Stream incision rate, age of strain marker
	Multiple samples in raised delta foresets	Relative sea-level curve, timing of marine limit
Burial dating/ isochron dating	Sediment in caves	Burial age of associated fossils, stream piracy
	Lava stack	Eruption recurrence rate
	Sediment buried under sediment	Age of paleoecological, paleontological, or anthropology records
	Cobbles buried by water	Duration of transgression
	Bedrock or sediment in glaciated area	Duration of cold-based ice cover
Erosion rate	Single rock surface	Outcrop-scale maximum constant erosion rate
	Single outcrop with TCN at saturation	Outcrop-scale average constant erosion rate
	Modern stream sediment	Average erosion rate for catchment above sample
	Older fluvial sediment	Paleo-erosion rates of catchment above sample
	Sediment sample	Erosion rate of surface with short-lived TCN
	Multiple samples in a depth profile	Erosion rate of sediment surface
	Two adjacent samples at different depth	Episodic erosion rate on glaciated summits
Paleoaltimetry	Single lava surface of known age with large vertical offset	Rate of offset
	Rapidly uplifted surface	Rate of uplift using atmospheric depth-dependent ratio of TCNs

sample mass) and our knowledge of production rate controlling factors such as atmospheric dynamics and the geomagnetic field variations over such a short integration time. Although the stable noble gas cosmogenic isotopes do not decay and have low thermal diffusivities in selected minerals at the Earth's surface, an effective upper dating limit on Earth is 10^7 years (e.g., alluvial surfaces in the Atacama Desert, Dunai et al. 2005). This is because the concentration of cosmogenic nuclides typically decreases with depth and because all surfaces on Earth over such long exposure durations will experience erosion. The applicable range for burial dating with ratios of TCN is narrower because short periods of shielding cannot be distinguished from the effects of erosion on the ratio.

The range of erosion rates over which the technique is applicable is narrow and depends on the approach, isotope-mineral system, and measurement precision. Surface erosion rates of continually exposed bedrock approaching 0.01 mm ka^{-1} can be determined with analytical precisions ($\sim 3\%$) and are usually averaged over a wide exposure time. Faster erosion rates, up to a maximum of 10^3 mm ka^{-1} for rock, may be resolved in the rare instance that the erosion rate is constant over much shorter exposure durations. Only recently has the TCN method been able to establish rates of the complex situation of nonconstant episodic erosion.

The TCN dating method extends beyond the normal limits of common Quaternary dating methods such as radiocarbon (5×10^4 years) and luminescence (10^5 years). Therefore, the technique provides a useful bridge between Quaternary and older dating methods. Furthermore, its ability to determine erosion and burial histories over the past 10^7 years can support exhumation models based on thermochronology.

Historical Developments

While the TCN dating method became established in the mid-1980s, the theory of the geochronometer was developed much earlier. Following the discovery of X-rays and radioactivity at the turn of the nineteenth century, experiments were undertaken to establish how high above Earth's surface atmospheric ionization would continue. As observation heights increased from towers to balloon experiments more than 5,000 m high in the atmosphere, it became apparent that above a few hundred meters the ionization rate actually increased with height and that the radiation did not diminish at night or during an eclipse. The demonstration of a non-terrestrial and nonsolar radiation (ionization with constant day and night and during an eclipse, Hess 1912) initiated a new field of physics. Two decades later, the first cosmic "radioelement" measured in rock was protactinium in eucolite and eudialyte, collected from surface outcrops in Greenland. Grosse (1934) carefully demonstrated that the amount of protactinium from the already well-established U-series decay rates was more than 3 % higher than the parent activity could explain. He indicated that a better understanding of the interaction of cosmic rays with matter and cosmic radiation variation with time was necessary to fully understand the production of cosmic radioelements. Knowledge of cosmic ray flux and interactions continued only through measurements of cosmogenic nuclides at higher concentrations in meteorites, lunar samples, and meteoric samples (tree rings, manganese nodules, ice sheets) and sophisticated transport codes capable of simulating particle interactions at various energies and magnetic field (Reedy et al. 1983). A current and very comprehensive review by Olive et al. (2014) provides the state of knowledge of the particle physics and cosmology underlying the theory.

Measurement of TCN lagged the theory. The low production rate of cosmogenic nuclides on Earth's surface even at mountain elevation (hundreds of atoms per gram of mineral per year) resulted

in few successful measurements of TCN (Davis and Schaeffer 1955; Hampel et al. 1975) until significant improvement in isotope mass spectrometry. Unlike radiocarbon dating (based on the decay of ^{14}C produced in atmosphere by cosmic rays and invented by Willard Libby in 1948), application of TCN methods has only been practical since the advent of improved spectrometry of noble gas isotopes and ultimately accelerator mass spectrometry (AMS) in 1977. The technical difficulty lies in the accurate measurement of an extremely small number of atoms, typically 10^6 to 10^8 in a sample that might range from a few milligrams ($\sim 10^{19}$ atoms) to a kilogram of material ($\sim 10^{25}$ atoms). Even after extracting and concentrating the chemical moiety of interest, say aluminum for ^{26}Al measurements, the isotopic ratios are still daunting, $<10^{-14}$.

During an experiment in which atmospheric ^{10}Be (half-life 1.39 Ma) was used as a radioactive tracer to prove that pelagic sediments from the ocean floor were carried through the subduction zone, and ultimately incorporated in the lavas erupted by arc volcanoes, Brown et al. (1982) obtained high concentrations (1×10^6 atoms g^{-1}) of ^{10}Be in the Columbia Plateau basalt. The Columbia Plateau basalt had been chosen as a control sample: since it was produced by hot-spot volcanism which has no connection with subduction, sediments, or any other “surface” material, it was expected to be a blank ($<10^2$ atoms g^{-1}). All other samples from hot-spot volcanism in Hawaii and Iceland had been blank. The significant difference between the Columbia Plateau sample and these other samples was that the other samples were collected within a year of their eruption, sometimes days, while the Columbia Plateau sample had lain subaerially exposed for 14 Ma. It was first thought that the ^{10}Be contamination might be meteoric ^{10}Be , brought to the basalt by rain. But sequential etching of the surface proved that the “contamination” was distributed uniformly throughout the sample. The only remaining possibility was that the ^{10}Be was produced in situ as the sample lay on the surface. A quick calculation showed it was possible. This was the first measurement of an in situ-produced terrestrial cosmogenic nuclide with modern methods. Shortly after, five papers in 1986 announced the birth of TCN exposure history and erosion methods (Craig and Poreda 1986; Klein, et al. 1986; Kurz 1986; Nishiizumi et al. 1986; Phillips et al. 1986). The number of different applications of the TCN method has continued to grow (Table 2; for reviews, see Lal 1991; Gosse and Phillips 2001; Dunai 2010; Granger et al. 2013).

Since Lal’s seminal 1991 paper, the number of parameters considered when interpreting the TCN data has increased, and uncertainty in their values has improved. During the last three decades, the community has benefitted from over a hundred studies from both individual and group efforts to improve sampling strategies, isotope geochemistry procedures, our knowledge of production rate through the atmosphere and lithosphere, and our capacity to process the data. The community shared a number of different calculators – e.g., CHLOE for ^{36}Cl ages, erosion rates, and depth profiles (Phillips and Plummer 1996), CosmoCALC for ages with any of the TCN (Vermeesch 2007), and a Bayesian-like Monte Carlo-based calculator for depth profile dating (Hidy et al. 2010). The most significant development began in the mid-2000s, when two multinational programs were funded for the primary purpose of improving our knowledge of TCN systematics. CRONUS-Earth was funded by the US National Science Foundation and CRONUS-EU was funded by the European Union. Early in the process, an online calculator was provided by members of the CRONUS-Earth group (Balco et al. 2008). Over the last decade, important data gaps were filled and improvements in our understanding were made in nuclear cross sections, radioactive decay rates, muonic interactions, spatial scaling of production rates, temporal variations in production rates, and a more robust assessment of error. The results of these programs have been recently published or submitted (Phillips et al. 2014 submitted). One major improvement is the manner in which the secondary flux is scaled through the atmosphere and the changing geomagnetic field (Lifton et al. 2014). An updated CRONUS online calculator is available at <http://web1.ittc.ku.edu:8888/>. Currently there

remains a lack of consensus regarding some aspects of the computation used in this and other calculators and the values of some of the parameters chosen, particularly the production rates. Although the CRONUS programs have ended, efforts to improve the TCN methods continue.

TCN Dating Systematics

TCN Production Pathways

At the base of the atmosphere, the most abundant secondaries capable of producing TCN are neutrons and muons. Other secondaries either lack energy, have rapid decay rates, are uncommon, or are absorbed so quickly in the atmosphere that they generate TCN at a much lower rate. TCN are produced in exposed minerals by three main interactions: spallation by high-energy neutrons, capture of thermal or epithermal neutrons, and muonic interactions.

At the base of the atmosphere, at sea level, the most abundant cosmic ray is muons with an average energy of 4.2 GeV. They have a vertical flux of $\sim 70 \text{ m}^{-2} \text{ s}^{-1} \text{ sr}^{-1}$ (for momentum $> 1 \text{ GeV c}^{-1}$); incident on a horizontal surface, the equivalent flux is $\sim 1 \text{ cm}^{-2} \text{ min}^{-1}$. Nucleons are the next most abundant: the integral vertical intensity of protons above 1 GeV c^{-1} is $\sim 0.9 \text{ m}^{-2} \text{ s}^{-1} \text{ sr}^{-1}$ and for neutrons $\sim 0.45 \text{ m}^{-2} \text{ s}^{-1} \text{ sr}^{-1}$. Other components of the flux including the electromagnetic pions and kaons play a little role in the production of TCNs.

Spallation

A spallation reaction occurs when a low-mass (e.g., neutron, proton) energetic ($> 30 \text{ MeV}$) particle interacts with a nucleus. The interaction causes an intranuclear or hadronic cascade that at first evaporates neutrons and protons and other light nuclei and then may eventually result in the breaking apart (fission) of the target nucleus. In general, the most probable products have masses close to the target nucleus or close to the projectile. All TCNs are produced by spallation, and it is the dominant production pathway for TCN within the upper $1,000 \text{ g cm}^{-2}$ ($\sim 4 \text{ m}$) of the lithosphere.

Thermal and Epithermal Neutron Capture

Neutron capture occurs when a slow neutron is absorbed by a nucleus to create a nucleus with a mass of one amu larger. Fast neutrons lose their energy through momentum transfer during elastic collisions with nuclei. Epithermal neutrons (0.1 MeV to 0.5 eV) and thermal neutrons ($< 0.025 \text{ eV}$) can be captured by a nucleus. The resulting nucleus is generally unstable and it decays by the immediate emission of a proton, or beta decay. Excited nuclei relax by emission of a gamma. While thermal-neutron capture is possible by many nuclides, the only cosmogenic nuclides that are produced significantly by thermal-neutron capture are $^{14}\text{N}(\text{n}, \text{p})^{14}\text{C}$, $^{35}\text{Cl}(\text{n}, \gamma)^{36}\text{Cl}$, and $^{40}\text{Ca}(\text{n}, \gamma)^{41}\text{Ca}$.

Muonic Interactions

Muons (leptons that are $207\times$ more massive than electrons) are produced in cosmic ray showers from the decay of mesons and comprise more than eighty percent of the non-electromagnetic cosmic ray flux at Earth's surface. However, like other leptons, they do not interact through the strong force and thus their penetration is much greater than neutrons. Despite their short half-life (10^{-6} s) and their relatively small contribution ($< 2\%$) to total TCN production at the lithosphere surface, slow negative muons (e -folding length $\Lambda \sim 1,300 \text{ g cm}^{-2}$, Heisinger et al. 2002a) and fast muon ($\Lambda \sim 4,320 \text{ g cm}^{-2}$, Heisinger et al. 2002b) are the dominant production pathways at depths greater than 4 m in rock ($> 1,000 \text{ g cm}^{-2}$). For comparison, the Λ for fast neutrons is $\sim 145 \text{ g cm}^{-2}$. Muon

contributions to TCN production are therefore important when applying TCN burial dating methods or when samples are collected from rock or sediment depths greater than 1 m.

TCN Production

Exposure duration (t) of a basalt boulder on a moraine is determined by the measurement of the TCN concentration in a target mineral, such as ^3He in pyroxene:

$$t = \frac{C_{meas} - C_i}{P_{T,t,0}} \quad (1)$$

where C_{meas} is the measured abundance of ^3He per gram of pyroxene, C_i is any concentration of ^3He that is either non-cosmogenic or in situ cosmogenic ^3He produced prior to the deposition of the boulder on the moraine (i.e., “inherited concentration”), and $P_{T,t,0}$, the total production rate at the surface, is the time-integrated sum of all cosmogenic nuclide production pathways for ^3He in pyroxene at the surface for the particular time, in atoms $\text{g}^{-1}\text{a}^{-1}$.

The state of knowledge of production rates and how they scale spatially and temporally is rapidly improving (Lifton et al. 2014; Phillips et al. 2014 submitted). Site-specific time-integrated production rates have been determined (calibrated) by measuring TCN concentrations in minerals with simple exposure histories over an independently determined duration (C_i is considered zero or is measured). The sum of production rates from the different cosmogenic nuclide interactions (fast neutrons, P_{nf} ; thermal neutrons, P_{nt} ; epithermal neutrons, P_{ne} ; negative muons, $P_{\mu n}$; and fast muons, $P_{\mu f}$) depends on the nuclide-target system, location, environmental factors, and the particular part of Earth’s geomagnetic field and atmosphere history corresponding to the exposure period. For reference, the calibrated TCN production rates are scaled to sea level, high latitude, under today’s geomagnetic and atmospheric conditions (e.g., ^{10}Be is produced in quartz at ~ 4 atoms $\text{g}^{-1}\text{year}^{-1}$). Thus, first-order (up to two orders of magnitude) adjustments to the reference production rate may be required to account for spatial variability in atmospheric and geomagnetic controls on the cosmic ray flux to any location on Earth.

Earlier simplifications with a symmetric standard atmosphere and dipolar magnetic field have now been replaced by more sophisticated models for both. In general, lower magnetic field strength will result in a higher production rate and a softer (lower average) secondary energy spectrum that will not penetrate as far. Sites at higher geomagnetic latitudes have higher surface production rates. The flux of each type of secondary decreases with penetration through the atmosphere, so production rates decrease with atmospheric depth. Atmospheric shielding is a greater control than geomagnetic field effects (except during reversals) so the highest production rates are at mountain tops.

The intensity and geometry of the geomagnetic field and the distribution of atmospheric mass has changed with time. The effects can cause changes of $>25\%$ over several millennia for a given site. Periods with higher paleointensities had lower instantaneous TCN production rates. During colder periods when the atmosphere contracted, production rates at high altitudes were less shielded. Such temporal variation in production is clearly evident from the variation in abundances of atmospheric ^{14}C or ^{10}Be abundances recorded in ice sheets or marine sediments. Fortunately, unlike the instantaneous effect of these changes on atmospheric cosmogenic nuclide production used for radiocarbon dating, terrestrial in situ production is integrated over the entire exposure duration, so TCN dating is not as sensitive to short-term high-amplitude geomagnetic or atmospheric variations.

Other first-order adjustments are needed to account for the decrease in production as the average energy of each type of secondary flux decreases with mass depth z (g cm^{-2}) through rock:

$$P_{z,nf} = P_{0,nf} e^{-z/\Lambda_{nf}} \quad (2)$$

where P_0 is the surface production rate and Λ_{nf} is the effective e -folding attenuation length for fast neutrons at that depth. While the concentration of TCN produced from spallation by fast neutrons generally follows this simple exponential, thermal-neutron capture interactions do not. Owing to the moderating effect of water (water vapor in air, pore water in rock or sediment, snow cover) on thermal neutrons, initially there is a reduced thermal and epithermal neutron flux in the upper 60 g cm⁻² of rock or sediment until the flux re-equilibrates with the exponentially attenuating fast neutron flux. Unlike spallogenic TCN, the highest concentration of thermal-neutron capture TCN occurs a few dm below the surface.

Second-order adjustments to the production rate may be negligible or significant. These include corrections for erosion or exhumation of the samples, cover by snow, water, ice, loess, or colluvium (shielding the surface from fast neutrons); geometry of the sampled surface; partial shielding by vegetation; elevation changes due to isostatic, tectonic, or surface processes; and partial shielding of cosmic ray secondaries due to topography.

Laboratory and Field Considerations

The field and laboratory procedures will depend on the objective of the study. Choices of TCN will mainly depend on the abundance of target minerals with known production rates, the radionuclide half-life, and whether or not multiple nuclides or a particular production pathway is sought.

There is no standardized list of field observations for TCN methods, partly because the types of TCN applications vary widely. Table 3 includes most of the important observations that will be needed to calculate an age or erosion rate, adjust for complexities in exposure history, interpret the data, and evaluate uncertainty. The number of samples necessary will depend on many factors. If inheritance is possible (e.g., due to exposure prior to the exposure period of interest), concordance of three or more surface exposure ages may be required to establish if inheritance is negligible, or subsurface samples in sediment collected in a depth profile may be needed to adjust for the average inheritance of a sediment.

While the physical and chemical processing required will vary with the isotope-mineral system, the objective is the same: provide a pure and representative target with sufficient TCN concentration to obtain the desired precision. Mineral isolation processes after cleaning, crushing, grinding, and sieving include froth flotation; magnetic, electrostatic, heavy liquid, air abrasion; and differential leaching with hydrofluoric, hexafluorosilicic, or hot phosphoric acid. For the noble gas measurement, no future chemistry may be required on the <100 mg of target mineral. For AMS, extracting and concentrating the radionuclides after dissolution is achieved with isotope dilution (spiking) followed by dissolution, ion chromatography, and pH-controlled precipitation, yielding BeO, Al₂O₃, AgCl, or other targets which are mixed with a pure metal to enhance sputtering in the AMS source. Masses between 2 and 200 g will be needed, depending on the concentration. Extraction of ¹⁴C is by thermal extraction of ¹⁴C in the presence of ultrapure O and can be in graphite or CO₂ gas. Most extraction methods require less than 10 g of quartz. Some elemental analyses of the naturally abundant isotope or a measurement of target nuclei abundances, radiogenic and nucleogenic sources, or neutron moderators is usually required.

Table 3 Field observations

Observation	Example	Comment
Latitude	-72.4472°	Convention: south is negative; high precision is useful for site recovery
Longitude	-130.3362°	Convention: west is negative; high precision is useful for site recovery
Elevation	3,232 m	Record method; evidence for surface elevation changes during exposure should be considered
Pressure	Varies	Used if atmospheric model does not adequately describe the time-averaged barometric pressure for the average temperature history
Bulk density	2.7 g cm^{-3}	Bulk density of the material sampled; if subsurface sampling, bulk density of the material above each sample must also be determined
Thickness	1.0 cm	Average thickness of the sample
Depth below top	0 cm or 10 g cm^{-2}	For surface samples, this is taken as 0 cm. For subsurface samples, the vertical distance between the landform surface and the top of the sample is recorded. Units vary with calculator
Surface slope	$19^{\circ} \rightarrow 235^{\circ}$	This is the dip and dip direction of the slope of the sampled surface. Generally dips less than 10° will have negligible foreshortening effects, unless there is considerable topographic shielding
Topographic shielding	235, 310, 40, 130, 170° 22, 13, 9, 17, 25°	Trend and plunge ($^{\circ}$) measurements taken at major topographic inflections in the skyline. This shielding becomes more critical with greater shielding (e.g., in a canyon) and with greater sampled surface slope
Sample height	130 cm; geometry	If the surface of the sampled landform is above the local ground level, such as a boulder top, it may be useful to provide the entire geometry (L, W, H) when considering neutron loss
Snow shielding	100 cm for 3 months, 50 cm for 2 months, 0.25 g cm^{-3}	An estimate of the thickness and density of snow that may have covered the sampled surface. If the surface is above the local ground level, consideration for the sample height may be required
Geometry effects	30 cm from edge; 25 cm under an overhang that protrudes 80 cm from cliff	This is needed to compute effective attenuation lengths, compute thermal-neutron production rates, and evaluate neutron loss
Forest shielding	Temperate rainforest for majority of time	Record the type of forest and other vegetation cover. For boulders, this could account for 2 % to >9 % shielding of secondary cosmic ray flux (e.g., boreal forest or temperate rainforest). For subsurface samples, vegetation shielding could be even greater
Erosion	1 mm ka^{-1} ; 30 cm max	If known, indicate method or evidence (height of protruding quartz vein; striation; soil development; lichen cover; weathering features; measured). Units vary with calculator
Aggradation	50 cm	Gradual or episodic cover by loess, ash, colluvium, ice, water, and other material currently or previously existing that was added to the surface of the landform after exposure began
Sample type	Boulder; braided stream deposits	Describe lithology, sediment structures

(continued)

Table 3 (continued)

Observation	Example	Comment
Landform type	Broad moraine ridge; fluvial terrace	Provide stratigraphy information, e.g., Qf3. Describe where on the landform the sample was collected (subsurface samples under a longitudinal bar in the alluvial fan)
Sample method	Cutoff saw; chisel; hand dug pit	Indicate any difficulties, particularly if thickness is not constant
Inheritance	High catchment erosion	Note evidence of catchment erosion for sediments (e.g., alluvial fans); low rates may indicate a higher probability of inheritance, yielding older apparent ages or causing scatter among individual ages on a given landform
Volumetric water	5 % water content in soil	The volumetric water content, Q_v , is needed to account for moderation of the thermal and epithermal neutron flux through rock and sediment. Each sedimentary layer and soil horizon may need its own measurement
Soil properties	15 cm below the 30 m mixed zone	Information about the soil that can help constrain erosion rate (e.g., a local catena, or evidence that the soil has been truncated); evidence that the samples were collected below any zone of cryoturbation or bioturbation; consideration that a soil horizon may have gradually altered the bulk density and moisture properties over time
Exhumation of the surface	Cobble may have been frost heaved, or till may have been eroded	Boulders and small clasts may have moved vertically in the sediment and been completely exposed for a shorter time than the actual landform. Exhumation by frost heave or denudation of the landscape should be noted

TCN Applications: Dating of Surfaces and Sediments with Simple Exposure Histories

Exposure dating has been conducted in just about every landscape element to address questions relevant to classical geomorphology, landscape responses to climatogenic and tectonic change, kinematics of brittle and ductile deformation, and applied science regarding geohazard risks associated with seismicity, volcanism, mass wasting, aridity, and sea-level change. Various combinations of isotopes and sampling strategies can reduce the degrees of freedom in constraining the factors that control the calculation of an exposure or burial age.

Single-Nuclide Surface Exposure Dating

A simple exposure age on a surface that is not eroding can be determined with a stable or radionuclide with decay constant λ :

$$t = -\frac{1}{\lambda} \ln \left(1 - \frac{C\lambda}{P} \right) \quad (3)$$

However, if the surface experienced a constant erosion or aggradation during the equation, it is more complicated. Constant erosion and aggradation can be treated explicitly. As the absorption of the cosmic ray secondaries with mass is well known, we are not required to sample at the surface. An approximation for the concentration of a nuclide in a rock at depth z (cm) with an erosion rate ε (cm a^{-1}) was provided by Lal (1991)

$$C_{(z,t)} = \frac{P_{(t,0)}}{\lambda + \frac{\rho\varepsilon}{\Lambda}} e^{-\frac{\rho\varepsilon}{\Lambda}t} \left(1 - e^{-\left(\lambda + \frac{\rho\varepsilon}{\Lambda}\right)t}\right) + C_{(z,inh)}e^{-\lambda t} \quad (4)$$

The latest CRONUS calculator ([Borchers et al. submitted](#)) iteratively seeks an exposure time with a set of equations that allow production rates through the five interaction pathways to vary over the exposure period, simultaneously considering changes in effective attenuation lengths during erosion. If erosion rate is known and constant, exposure age can be solved. However, if the erosion rate is uncertain or appears to be episodic, the normal protocol with a dominantly spallogenic TCN is to assume $\varepsilon = 0$ to obtain a minimum exposure age for the surface. If the inherited concentration ($C_{(z,inh)}$) is also not negligible, but erosion is zero, the exposure age would be a maximum age. The exposure age cannot be constrained with one isotope (maximum nor minimum limit) if both inheritance and erosion are nonzero. However, if single-nuclide exposure ages from multiple, spatially distinct samples from the same landform are identical, then it may be possible to suggest a negligible inheritance in all samples.

Multiple Nuclide Surface Exposure Dating

To overcome the difficulty related to erosion, two nuclides can be measured in the same rock surface. If the surface has been exposed and eroding at a steady state for a long time, the concentration of radionuclides will reach a dynamic equilibrium where loss due to decay is matched by the production according to the above equation. A short-lived radionuclide that has reached its saturation concentration C^* for a given erosion rate over sufficient time can be used to determine the erosion rate (Lal [1991](#)):

$$\varepsilon = \frac{\Lambda}{\rho} \left(\frac{P}{C^*} - \lambda \right) \quad (5)$$

The surface exposure time can be determined by adjusting the unsaturated concentration of a second nuclide for this erosion rate. Alternatives to the saturation approach include a combination of a TCN with a significant thermal-neutron capture production rate (e.g., ^{36}Cl) and a spallogenic isotope (e.g., ^{10}Be). The thermal-neutron loss near the surface will cause the concentration to increase with erosion, while the spallogenic nuclide will decrease for the same erosion rate. Their erosion-adjusted ages will converge provided that erosion rate is not too fast and that sufficient ^{35}Cl is in the mineral.

The two-isotope approach can also solve exposure age and erosion rate simultaneously for two radionuclides without the need for saturation or thermal-neutron production (Fig. 2). However, the $^{26}\text{Al}/^{10}\text{Be}$ ratio plot (Nishiizumi et al. [1986](#)) reveals a narrow banana-shaped steady-state island and therefore requires very high precision to establish erosion and exposure age. Phillips et al. ([1997](#)) have suggested that the $^{10}\text{Be}/^{36}\text{Cl}$ may have the advantage of being more sensitive for experiments requiring simultaneous solutions of exposure age and erosion rate. Ratios of a noble gas and radionuclide have also been used, and a three-isotope approach may have the advantage of a reduction of a degree of freedom. The multi-isotope approach may also simplify the requirement to know how production rates have changed with time if, in some circumstances, the amount of variation is the same for all measured isotopes in the same sample.

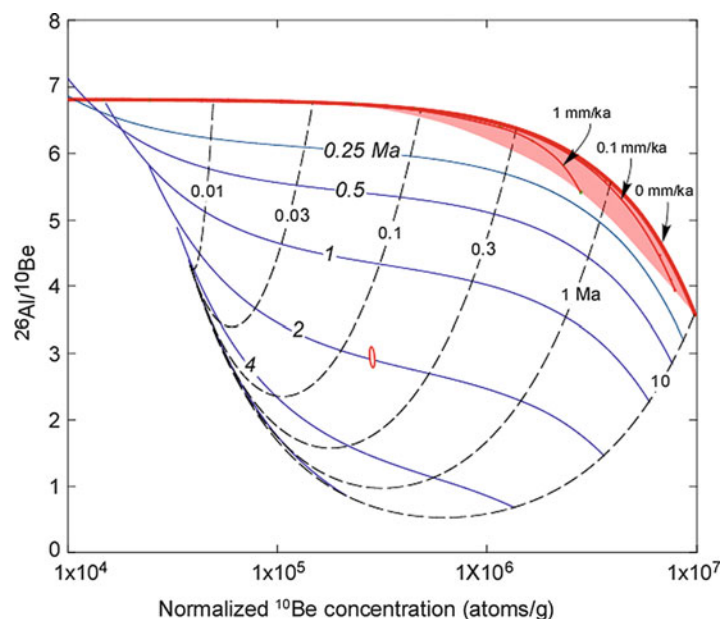


Fig. 2 $^{26}\text{Al}/^{10}\text{Be}$ versus ^{10}Be plot. Production systematics as per Balco et al. (2008) for the Lal (1991) and Stone (2000) time invariant scaling model, initial ^{10}Be production rate of 4.9 atoms g^{-1} and surface $^{26}\text{Al}/^{10}\text{Be}$ of 6.75, and muogenic production from negative and fast muons (Heisinger et al. 2002a, b). Plot and sample represent a surface of 30 m depth under gravel with 1.9 g cm^{-3} density. The thick red upper curve represents the history of a sample that experienced continuous exposure with no erosion (exposure duration in Ma increases to the right). Ratios plotting within the shaded field (“steady-state erosion field” (Lal 1991)) have experienced erosion or minor burial (curves indicated for 0.1 and 1.0 mm ka^{-1} constant and continuous erosion). Samples plotting below the shaded field have experienced a complicated exposure history in which an exposure was by at least interrupted one burial event. Even at 30 m, the shielding is not complete because of muogenic production. The duration of burial indicated by the thin blue curves ranging from 0.25 to 8 Ma represents the burial age for a single even or a minimum estimate of burial duration if multiple burial events have occurred, as in cyclic glacial cover. The hypothetical sample shown with 1σ error ellipse could be interpreted to represent a minimum exposure duration of 0.2 Ma and minimum burial duration of 2 Ma. However, it is possible that the sediment was buried and reexposed many times, so the total time represented would be greater than 2.2 Ma. If an amalgamated sediment had a depressed initial ratio (owing to complex exposure prior to final deposition), then the burial age would overestimate the timing of the last burial event

Exposure Dating of Sediments

The difference between dating the exposure age of a rock surface and dating the depositional age of a sediment is that each grain of the allochthonous sediment will have a different C_{inh} which must be considered in the calculations. There are many approaches to dating a sediment (see Gosse 2012 for a review). If the objective is to determine the age of a cut or fill alluvial terrace surface, a fan or delta surface, moraine, or mass wasting deposit, it is possible to date large boulders (reducing the effect of snow or loess cover and exhumation) or cobbles and pebbles on the surface. As in dating a bedrock surface, a single-nuclide age on a clast (or amalgamation of clasts) on the surface of a deposit requires knowledge of erosion (or aggradation) history and inheritance.

Erosion of the surface can be determined by different TCN approaches as discussed above. An alternative approach is to use subsurface samples. The concentration versus depth profile through a rock or sediment is controlled by erosion rate. The faster the erosion rate, the steeper the profile until ultimately only a fast muonic attenuation would be measured. Unfortunately, constant erosion rates on Earth are generally not that fast, so most measured depth profiles will be dominantly controlled by the simple e -folding length for a fast neutron. Therefore, a single spallogenic nuclide cannot establish a unique erosion rate or exposure age. However, a depth profile for a single TCN with

sufficient thermal-neutron capture production (e.g., ^{36}Cl) can provide this uniqueness. Alternatively, two TCNs can be measured in the same profile to solve for erosion rate and age (Mercader et al. 2012).

The C_{inh} in sediment clasts is equally problematic. If not treated, the apparent exposure age will overestimate the actual timing of deposition. There are many approaches, each with assumptions that may be validated in certain scenarios. One option is to measure the exposure age for many samples on the surface of the deposit and assume that all clasts have been eroded similarly. If there is no variability among ages, then it may be possible to interpret that inheritance is negligible, as it is very unlikely that all clasts would have the same inheritance if the C_{inh} was a significant component of the total concentration. This is often the case where sediment is eroded from glaciated catchments or regions with otherwise very high erosion rates. In regions where the sediment is sourced from a catchment that has not been rapidly eroded, determining the C_{inh} is necessary. One option is to measure a sample that is essentially shielded from cosmic rays (e.g., $>4,000 \text{ g cm}^{-2}$ deep) for long exposure to muons (Brown et al. 2002) and assume that the sediment at shallower depths have the same C_{inh} . This assumption would only be true in special cases where, for instance, the sediment flux from the catchment remained constant over that entire thickness. A similar approach that uses the TCN concentration in modern stream sediment as an indication of C_{inh} is similarly invalid for many catchments in which millennial-scale climate variations have changed catchment erosion rates. A better and more widely used treatment of inheritance in alluvium (Anderson et al. 1996) uses the TCN concentration in at least four subsurface samples of amalgamated clasts along a depth profile. The profile will reveal the time-integrated concentrations from the different interaction pathways as the rock is advected toward the surface due to erosion. The exponential decrease in concentration will trend toward zero with depth if there is no inheritance. However, if C_{inh} is nonzero, the concentration versus depth curve will be asymptotic along the depth axis. The offset corresponds to the C_{inh} and can be subtracted from the measured concentration to solve for erosion or exposure age. Hidy et al. (2010) showed that amalgamations of hundreds of thousands of sand clasts provide a more precise solution than dozens of pebbles (pebbles seem to work in rapidly eroding catchments, whereas many more sand grains are necessary to characterize the average C_{inh} where catchment erosion rate is low, and C_{inh} is high and more variable).

Burial Dating

When rock or sediment is buried and effectively shielded from any secondary cosmic ray flux, the concentration of TCNs in the buried minerals will change according to their decay rate. The noble gases will remain constant (assuming no unaccounted diffusion) and radionuclides with faster decay rates will decrease faster. The change in the ratio of the concentration of two (or more) different TCNs in the same sample, as long as one is a radionuclide, depends on burial duration, erosion rate, and depth. Burial dating has been contributed to many different disciplines:

- Glaciology and paleoclimatology: burial of bedrock by one or more episodes of glacier cover (e.g., Nishiizumi et al. 1991)
- Anthropology and archaeology: sediment and associated human fossils that were shielded in caves (e.g., Shen et al. 2009)
- Geomorphology and paleontology: fluvial terraces and alluvial back to the Pliocene (e.g., Rybczynski et al. 2013)

Simple Burial Dating with Two Isotopes

In the simplest case of a surface that had build up over exposure time (t) interrupted by a single period of complete shielding from cosmic rays (t_b), the burial duration can be determined using two TCNs with different mean lives (τ) in the same sample:

$$t_b = -\frac{\tau_{\text{short}}\tau_{\text{long}}}{\tau_{\text{long}} - \tau_{\text{short}}} \ln\left(\frac{P_{\text{long}}(t, z, \varepsilon)C_{\text{short}}}{P_{\text{short}}(t, z, \varepsilon)C_{\text{long}}}\right)$$

where C is the measured concentration and $P_{(t,z,\varepsilon)}$ is the sum of the time-averaged production rate over the time of exposure for a given depth and erosion rate for the short- or long-lived isotope (Granger and Muzikar 2001). In this simple scenario, such as burial of a lava by another thick lava, there $C_{\text{inh}} = 0$ atoms g^{-1} and $\varepsilon = 0$ cm a^{-1} . Even if the initial exposure duration is not known, the pre-burial and burial durations may be solved if the ratio of the two isotopes fall below the steady-state island in a ratio plot (e.g., $^{26}\text{Al}/^{10}\text{Be}$ vs. ^{10}Be , Fig. 2), erosion is assumed negligible, and the surface or sediment had never experienced a previous burial (or storage) event. This method requires two isotope measurements in only one sample. It assumes that burial was complete and instantaneous; otherwise, production during partial exposure at varying depths with time will need to be considered.

Isochron Burial Dating

Balco and Rovey (2008) provided an isochron solution for the common instance where a surface or sediment has undergone previous burial episodes. In these cases, the initial ratio of the isotopes measured in a sample does not correspond to the concentration for the production ratio $\left(\frac{P_{\text{short}}(t, z, \varepsilon)}{P_{\text{long}}(t, z, \varepsilon)}\right)$.

Instead, prior burial durations will cause the concentration ratio to be lower at the beginning of the last burial episode. If ignored, the calculated burial duration will overestimate the burial age. By using an isochron approach (Fig. 3), the concentration ratio prior to the last burial episode does not need to be known. The isochron approach requires that multiple samples are collected in the buried rock or sediment and that the concentrations of the TCN in each sample are different but that the ratio of the two TCN samples is the same. One option is to collect samples within a short (<1 m) depth profile interval below the burial contact. In this case the concentration for each TCN will diminish with depth if the buried minerals were exposed prior to burial. The greater the pre-burial exposure time, the greater the differences in concentration in the samples. However, the ratio of two spallogenic nuclides will be approximately constant over this short and shallow interval. For instance, on a $^{26}\text{Al}/^{10}\text{Be}$ isochron plot, the initial slope will be close to the production ratio (~ 6.75). During burial, the isotopic ratios will decrease at a rate proportional to their concentration, so the slope of their concentrations will decrease. The slope is proportional to the burial duration. In instances where exposure prior to burial was short (e.g., if eruption recurrence intervals were short) or there is no evidence of a paleosol because of significant erosion prior to burial, there are other options for obtaining multiple samples with different concentrations. For instance, there is a well-documented grain size dependency on concentration in sediments where deep-seated landsliding has occurred (Brown et al. 1995), so ^{26}Al and ^{10}Be concentrations in different grain size fractions from a single sample may be sufficiently distinct to define a ^{26}Al versus ^{10}Be slope.

In the instance that multiple burial events have occurred, such as on a glaciated summit, different approaches have been used to constrain the possible burial history. The approaches use a combination of burial dating with two or more TCNs and an independent record of glaciation, such as an ice volume time series from a marine or ice sheet record. A recent approach reported by Margreth

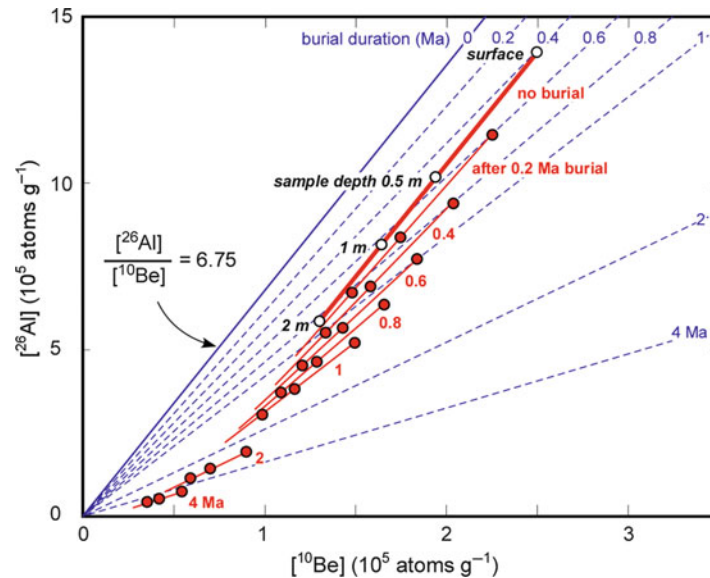


Fig. 3 Concept of TCN burial isochron dating (Balco and Rovey 2008), illustrated using a $[^{26}\text{Al}]$ - $[^{10}\text{Be}]$ plot. The ratio of samples collected from a continuously exposed soil (never buried) will plot on the *solid blue curve* depending on depth and exposure duration. *Blue dashed curves* represent sediment in a paleosol that was buried once (continuously) for the indicated duration. *Red curves* are defined by samples collected at different depths in sediment that had previously experienced burial and was redeposited and weathered in the modern paleosol. The initial ratios of the red samples in the paleosol would be less than the production ratio of the isotope pair (6.75 in the case of $^{26}\text{Al}/^{10}\text{Be}$). The slope and position of the isochrons solve for initial ratio and burial duration simultaneously

et al. (submitted) used the ratio of two radionuclides in two nearby surfaces, but one has been more recently plucked than the other. Considering periodic burial by ice, and even subaerial and episodic subglacial erosion, the concentrations and ratios help constrain the long-term (millions of years) fraction of ice-free time.

TCN Applications: Erosion Rates

While erosion can contribute significantly to the uncertainty of exposure ages, the dependence of concentration on erosion increases the value of the TCN method. The TCN method can provide a direct estimate for erosion rate of local surfaces to large catchments. Erosion rates on bedrock surfaces have provided a means to establish background rates for comparison with recent erosion rates during the Anthropocene, or longer-term rates determined by thermochronology, or relief generation from the difference between valley and summit erosion rates.

In most applications of TCN erosion rate analysis, the overriding assumption is that the erosion was continuous and constant over the entire exposure duration. A single concentration in one sample on a surface constrains erosion (Eq. 5) if the radionuclide has reached its saturation concentration C^* . Saturation can be achieved more easily by using a short-lived isotope (e.g., ^{14}C) on a rapidly eroding surface (e.g., a sloped surface on a sediment, Fig. 1). If the objective is to obtain an estimate of erosion over a longer time period than recorded by a short-lived TCN, but the C^* for the longer-lived isotopes has not been attained, then the erosion rate determined from Eq. 5 will be an estimate of the maximum erosion rate permitted to achieve the measured concentration. Multiple nuclides measured in one sample can provide the exposure duration and erosion rate of that surface (e.g., Nishiizumi et al. 1991; Phillips et al. 1997).

It is also possible to apply Eq. 5 to estimate the denudation rate of an entire catchment. While the approach was first conducted using meteoric ^{10}Be absorbed on regolith delivered to streams (Brown et al. 1988), the method now uses the lower concentrations of in situ TCN in the same sediments (Brown et al. 1995; Granger et al. 1996). The approach assumes that at each location in a catchment, the concentration at the surface has reached saturation. However, instead of tagging the C^* and therefore ε at every surface in the basin, the hillslope processes and streams will deliver a flux of sediment that is scaled with the erosion rate of the upstream slopes. Thus, one sample of modern stream sediment provides an estimate of basin-average erosion rate for all catchment surfaces above that point. A basin TCN production rate can be calculated by taking the average of production rates for each pixel in the DEM; scaled for latitude, longitude, and elevation; and adjusted for topographic shielding, vegetation, and other factors. The basin-average erosion rate method relies on the constant delivery of sediment from all surfaces in the catchment and assumes a homogeneous distribution of the mineral of choice. Special approaches are required if some areas of the catchment are not eroding or have no target mineral of the selected grain size. The duration over which the erosion rate is applicable depends on the radionuclide decay rate and the erosion rate of the catchment (faster rates reduce the averaging time).

It is also possible to determine the paleo-erosion rate of a basin (Schaller et al. 2002; Hidy et al. 2014). Instead of using modern sediment, it is necessary to sample sediment stored in the catchment that was deposited at the time of interest. In order to obtain the average depositional concentration (C_{dep}) for a given time in the past, we determine the inherited concentration (C_{inh} , e.g., with a depth profile) and compensate for the concentration lost to decay over the time since deposition. Time since deposition may be determined with TCN methods or independently with a different dating method. The method assumes that any changes in catchment elevation, relief, area, or target mineral abundance with time are negligible or known.

Uncertainty and Assumptions of TCN Exposure Ages and Erosion Rates

Arguably more than any other dating method described in this encyclopedia, the TCN dating method is more sensitive to sample and environmental context. For this reason, it is challenging to establish a rigorous analysis of total uncertainty in an exposure age, burial age, or erosion rate (Borchers et al. submitted). There is no consensus on whether or not 1σ or 2σ uncertainties shall be reported. In some instances involving Monte Carlo approaches, the only fits obtainable are at the 3σ level and that error is not reduced to a lower confidence level.

Internal random errors affect the precision of the measurement. These include (i) AMS or MS precision (typically based on a Poisson distribution, averaging 2–3 % 1σ), (ii) uncertainty in the spike or carrier concentration (generally better than 2 % 1σ), and (iii) contribution to the measurement of the process blank, calculated by considering what fraction of the sample measurement was contributed by the process (usually <1 % except for very low-level measurements). As ^{36}Cl requires elemental analysis of potential target elements, and thermal-neutron absorbers and producers, the uncertainty in ICP, ICP-MS, or XRF measurements is also incorporated.

The principal external error is uncertainty in the scaled and time-averaged production rate. Balco et al. 2008 recommended approximately 10 % 1σ uncertainty, and it is unclear if the production rate uncertainty has improved for each TCN since then.

Most publications do not consider the other sources of error that relate to the various environmental conditions that affect production rate or add complexity to the exposure and burial history. In the newest CRONUS-Earth online calculator, uncertainties for all of the required input parameters

are requested, including uncertainty in the shielding factors for snow, vegetation, geometry, topography, and effective attenuation lengths. Hidy et al. (2010) also incorporated the stochastically or normally distributed uncertainties in bulk density and inheritance in evaluating error for depth profile ages and erosion rates. Still typically non-quantified are errors associated with surface uplift, erosion, episodic erosion, burial and aggradation, exhumation, mixing, and other factors.

Numerous comparisons of TCN surface exposure ages of rock surfaces and sediments and other dating methods have been published, and summaries of recent interlaboratory comparisons and duplication measurements have been reported in Jull et al. (2013) and Phillips et al. (2014 submitted). These include alluvial depositional ages against OSL in the same section, erratic boulder exposure ages against calibrated radiocarbon ages, and exposure ages on lava dated with $^{40}\text{Ar}/^{39}\text{Ar}$.

Assumptions Common to Many TCN Dating Applications

- The TCN production rate is known for a given production pathway. This is the major source of uncertainty in the dating method. The production rate varies as a function of (i) temporal and spatial variations in dipole and non-dipole magnetic field controls on the GCR flux to the atmosphere (Lal 1991; Lifton et al. 2014), (ii) temporal and spatial variations in atmospheric shielding of GCR and secondaries (Lal and Peters 1967; Stone 2000; Staiger et al. 2007), and (iii) depth below the surface because of attenuation of the cosmic ray flux through different interactions that depend on the energy spectra and type of secondary and the chemistry of the mineral matter.
- All cosmogenic, radiogenic, and nucleogenic pathways are recognized. For TCN exposure dating the primary cosmogenic production pathways are spallation, capture, and muonic interactions (Lal 1991; Gosse and Phillips 2001).
- Any initial TCN concentration prior to the exposure of interest is negligible or can be determined independently, e.g., with depth profiles through sediment (Anderson et al. 1996).
- The cosmic ray flux is constant. The uncertainty in this assumption has not been well established (e.g., Wieler et al. 2013).
- TCN concentrations are measured accurately. While the majority of modern measurements with noble gas mass spectrometers or accelerator mass spectrometers (AMS) average 2–4 % 1σ precision for some TCN (Vermeesch et al. 2012; Jull et al. 2013), the actual range of internal measurement precisions evaluated by duplicates and interlaboratory comparisons can be larger. Low TCN concentrations due to small sample mass, low production rate, short exposure time, or long burial time will increase uncertainty because of counting statistics (Poisson distribution), the uncertainty in blank correction (by nature, the process blanks will have poor counting statistics), spectrometry detection limits, and, in the case of AMS, normalization with standards with TCN abundances that are more than two orders of magnitude greater than the low-level samples.
- No unaccounted surface processes have influenced the exposure or erosion history of the minerals being dated. For instance, there is negligible or known effects of (i) erosion of the rock surface (Gillespie and Bierman 1995); (ii) shielding and the moderating effects of snow (Gosse and Phillips 2001; Zweck et al. 2013; Delunel et al. 2014), soil moisture (Dunai et al. 2014), ice, or forests and vegetation (Plug et al. 2007); (iii) exhumation (Putkonen and Swanson 2003); and (iv) movement of the dated material by tectonics, isostasy, mixing, or rotation during exposure.

Cross-References

- ▶ [Accelerator Mass Spectrometry \(AMS\)](#)
- ▶ [Erosion Rate \(Cosmogenic\)](#)
- ▶ [Glacial Landscape \(Cosmogenic\)](#)
- ▶ [Meteoritic \(\$^{10}\text{Be}\$ \)](#)
- ▶ [Meteorites \(\$^{36}\text{Cl}\$ \)](#)
- ▶ [Noble Gas Mass Spectrometry](#)
- ▶ [Radiocarbon Dating](#)
- ▶ [River Terraces \(Cosmogenic\)](#)
- ▶ [Rock Surfaces \(Cosmogenic\)](#)

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Radiocarbon Dating of Marine Carbonates

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Definition

Contaminant: Carbon-containing materials that do not originally belong to the sample.

Pretreatment: A process applying physical and chemical treatments to remove contaminants.

Contamination and Sample Pretreatment

Marine carbonates such as shells and corals mainly consist of aragonite. Before samples are processed for radiocarbon dating, all contaminants must be removed; otherwise the determination of correct radiocarbon ages may not be achieved. Contaminants are derived from the surrounding environment if samples were buried in soils or sediments (e.g., secondary carbonates derived from groundwater and recrystallization of sample carbonate due to chemical exchange between the sample and the surrounding environment). These carbonate contaminants are mostly in the form of calcite. Contaminants can also be conservation materials in the case of museum specimens. Contamination cannot always be seen by naked eye. In such cases, samples should be screened for secondary carbonates and recrystallization and diagenetic alteration using X-ray diffraction, thin-section examination (McGregor and Gagan 2003), or scanning electron microscopy (Webb et al. 2007; Nothdurft and Webb 2009).

If the outer layers of carbonate samples are contaminated by secondary carbonates, the outer surface of the samples is usually cleaned physically by abrasion or sandblasting and/or chemically by acid etching. Routine pretreatment of shell samples involves removal of the outer 20 % (by weight) of the samples by acid etching (Walker 2005). If contamination appears not only in the outer layers but also in the inner layers of carbonate samples (e.g., recrystallization and diagenetic alteration), acid etching may not be useful. This pretreatment method may result in an increase of the proportion of diagenetic calcite in the samples because aragonite is more soluble than calcite in acid media (Douka et al. 2010). This means poorly preserved carbonate samples may not be adequate for ^{14}C dating. Recently, Douka et al. (2010) and Russo et al. (2010) have tried to separate original aragonite from diagenetic calcite of poorly preserved fossil shells and corals by density separation using lithium heteropolytungstate and bromoform, respectively. Their initial test results were very encouraging.

Pretreated samples free of contamination are converted to CO_2 by reaction with acid solutions (dilute HCl or 85 % H_3PO_4). The sample CO_2 is usually converted to benzene or graphite for radiocarbon analysis using radiometric and accelerator mass spectrometry (AMS) method, respectively (Walker 2005; Hua 2009; Sloss et al. 2013).

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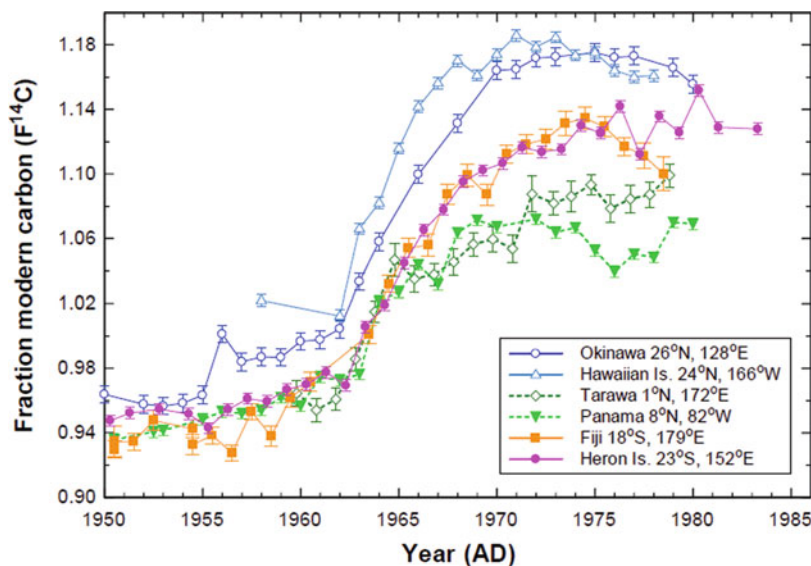


Fig. 1 The ^{14}C content in the surface waters of the Pacific Ocean for the period 1950–1984 recorded in corals. Error bars are 1σ (Adapted from Hua (2009))

Marine Reservoir Effect and Age Calibration

After its production in the atmosphere, radiocarbon is oxidized to $^{14}\text{CO}_2$. In this form, ^{14}C is transferred from the atmosphere to the surface ocean via air-sea gas exchange and then incorporated into the deep ocean. The residence time of carbon in the deep ocean is quite long (~ 800 – $1,000$ years), and during this time ^{14}C in deep ocean waters decays without replenishment from the surface. As a result, the deep ocean has a much lower ^{14}C content than that of the atmosphere, or materials drawing carbon from the deep ocean reservoir are much older than contemporaneous materials of terrestrial origin. For the surface ocean, the aging effect is smaller because the surface ocean, exchanging with both the atmosphere and the ^{14}C -depleted deep ocean, has a ^{14}C level intermediate between these two reservoirs. In other words, marine organisms living in the surface ocean (e.g., shells, corals, and planktonic foraminifera) appear older than contemporaneous terrestrial samples. The age offset between surface ocean and terrestrial samples, ~ 400 years on average, is known as the marine reservoir age (R). Marine reservoir effect is corrected during the process of age calibration.

As radiocarbon and calendar ages are not the same, the former ages have to be converted to the latter ones using an age calibration process. To calibrate a radiocarbon date for a surface ocean sample, one can use an internationally ratified terrestrial calibration curve (e.g., IntCal13 for the Northern Hemisphere (Reimer et al. 2013) or SHCal13 for the Southern Hemisphere (Hogg et al. 2013)) with a known value of R . Alternatively, one can use the current internationally ratified marine calibration curve Marine13 (Reimer et al. 2013) with a known value of regional offset from the global marine model age for that sample, defined as ΔR . The latter method is generally preferred. Databases of R and ΔR values for different regions are available online (e.g., <http://calib.qub.ac.uk/marine/> and <http://radiocarbon.ldeo.columbia.edu/research/resage2.htm>). Calibration of ^{14}C ages is undertaken using a computer program. Several programs are available online (e.g., CALIB at <http://radiocarbon.pa.qub.ac.uk/calib/>, OxCal at <http://c14.arch.ox.ac.uk/embed.php?File=oxcal.html>).

Dating of Recent Materials

Atmospheric nuclear weapon tests, mostly in the late 1950s and early 1960s, released a considerable amount of ^{14}C into the atmosphere, leading to an enormous increase in atmospheric ^{14}C concentration. Via air-sea exchange of CO_2 , ^{14}C levels in the surface ocean also increased significantly. This means bomb radiocarbon can also be used to date recent marine carbonate samples. However, unlike the simple zonal pattern of bomb ^{14}C in the atmosphere (Hua et al. 2013), the distribution of bomb ^{14}C in the surface ocean is sensitive to local and regional patterns of ocean circulation including horizontal advection and vertical transport such as ocean upwelling. In other words, ^{14}C levels in the surface ocean have local and regional characteristics such as those depicted in Fig. 1 for the Pacific Ocean. Therefore, recent marine carbonate samples from a particular location can accurately be dated only if a surface ocean bomb ^{14}C curve for such location/region, which serves as a radiocarbon calibration curve, is well determined. Based on Fig. 1, the highest dating accuracy can be achieved for marine organisms formed in the period from ~1960 to the mid-1970s, when there was a significant increase in surface ocean ^{14}C .

Advances in Dating of Marine Carbonates

Small quantity of materials required by the AMS method (tens of micrograms to a couple of milligrams of carbon; Hua 2009; Sloss et al. 2013) has advanced radiocarbon dating in general and dating of marine carbonates in particular. For example, depositional chronologies of reef islands are traditionally based on radiocarbon dating of bulk carbonate sediments using the radiometric or conventional method. However, Woodroffe et al. (2007) dated by AMS different skeletal components of carbonate sediments (corals, foraminifera, and gastropod shells) collected in a transect across Warraber Island in Torres Strait (Australia) and compared these AMS dates to those of corresponding bulk carbonate sediments. The authors found that gastropods appeared to be the youngest among the samples and concluded that ^{14}C dates on the most dominant skeletal organism (gastropods in this case) rather than those on bulk carbonate sediments should deliver reliable information on reef island evolution.

The ability to analyze microgram-sized samples by AMS also helped to answer one of the important questions on the study of reef islands: How quick after their death are skeletal organisms transported from reef flats, where they are produced, to deposit to build reef islands? This question becomes more important as climate change progresses. In this scenario, the oceans become more acidic due to their uptake of anthropogenic CO_2 ; therefore it is likely that the skeletal organisms are vulnerable and consequently the development of reef islands is unsustainable. Dawson et al. (2013) studied Raine Reef in northwestern Australia and dated individual foraminifera, the most dominant skeletal organism at Raine, at different locations including the reef flat and beaches. A surface ocean ^{14}C bomb curve for the study region derived from known-age corals was reconstructed to facilitate the dating of these recent foraminifera. The AMS results on pristine samples indicated that it took a short period of time (maximum of 13–27 years) to transport the samples from the reef flat to the island, over distance up to 2 km.

Another example of dating of small-sized carbonate samples is the use of bomb ^{14}C in the surface ocean to validate fish ages (Ewing et al. 2007; Andrews et al. 2011). This method was pioneered by Kalish (1993) when he showed a good comparison between ^{14}C values recorded in known-age otolith carbonate of a marine fish species and regional surface ocean ^{14}C records from corals of the Great Barrier Reef. In this application, the birth dates of fish specimens were first

estimated by counting annual increments visible in otolith thin sections. These dates were then checked or validated by comparing the ^{14}C content of the first annual otolith increment with a regional surface ocean ^{14}C bomb curve.

Difficulties in Dating of Marine Carbonates

The ^{14}C content in some shellfish species may not reflect that of dissolved inorganic carbon (DIC) of surrounding sea waters at the time of accretion of their calcium carbonate skeletons, leading to problems in radiocarbon dating of these species. Petchey (2009) attributed these issues to the dietary and habitat preferences of shellfish. In particular, deposit feeders consume detritus in areas dominated by limestone geologies containing much older carbon or digest younger carbon from a terrestrial source in areas influenced by local freshwater runoff. As a result, the ^{14}C ages of these shellfish samples are older or younger than the true ages, respectively. Dating of carnivorous shellfish is also problematic because of the uncertainty in their ^{14}C content, which is dependent on the carbon reservoirs of their prey. By contrast, suspension feeders, which consume suspended phytoplankton and seawater DIC, reflect the ^{14}C content of the surface ocean and are therefore considered as the most reliable shellfish for dating (Petchey 2009).

The ^{14}C content of organisms living in atoll lagoons and estuaries may also be different from that of open ocean waters. For shallow lagoons with limited exchange with open ocean waters, ^{14}C levels of lagoonal waters are strongly influenced by air-sea gas exchange and are therefore much higher than those of nearby open sea waters (Petchey 2009). Similarly, ^{14}C levels of estuarine waters reflect the interaction and mixing of terrestrial and marine carbons (Ulm 2002). The estuarine effect is significant where water circulation is restricted. Thus accurate dating of these organisms can be achieved only if R and/or ΔR values relevant to their environment are known.

Radiocarbon dating of surface ocean samples involves estimates of marine reservoir effect (R and ΔR). These values for a given location are generally assumed to be constant with time when calibrating marine ^{14}C ages. However, recent studies have reported large variability in the marine reservoir effect of several hundred to a couple of thousand years for various regions during the Late Glacial and Holocene (e.g., Siani et al. 2001; Bondevik et al. 2006; Yu et al. 2010; Ortlieb et al. 2011). These variations resulted from changes in ocean circulation and the carbon cycle associated with climate change. For these regions, if temporal variability in R and ΔR does not take into account when calibrating marine ^{14}C ages, the resultant calibrated ^{14}C ages may be erroneous. Ortlieb et al. (2011) reported high ΔR values for the northern Chile-southern Peru coast of up to 1,000 years during the period 7,000–10,000 cal years BP (early to mid-Holocene) in comparison with their modern value of 200–300 years. The authors showed that the calibrated ^{14}C ages during the early to mid-Holocene based on the constant modern ΔR value were older than the true calendar ages of up to 800–1,000 years.

Summary

Radiocarbon dating has widely been used to reconstruct chronologies for marine carbonates for the past 50 ka for studies in archaeology, earth sciences, paleoceanography, marine ecology, and Quaternary climate change. For example, radiocarbon-dated corals have been used to investigate changes in sea surface temperature and salinity, and variations in El Niño-Southern Oscillation through time. Radiocarbon dates on boring bivalves occurring in dislocated boulders and on

mollusk shells associated with gravel deposits along coast lines have also been employed to constrain the timing of tsunami events. In addition, radiocarbon dating of cultural shells has been used for the study of human occupation and colonization of Pacific atolls.

With the advent of AMS radiocarbon dating on microgram-sized samples, some radiocarbon applications are available (e.g., validation of fish ages by ^{14}C analysis of fish otoliths) or become more reliable (e.g., ^{14}C -based chronologies for the study of reef island evolution). However, the dietary and habitat preferences of shellfish, the lagoonal and estuarine effects, and possible temporal variations in the marine reservoir effect should be carefully considered when dating marine samples.

Cross-References

- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Bomb Carbon](#)
- ▶ [Geochronology](#)
- ▶ [Otolith](#)
- ▶ [14C Dating](#)
- ▶ [Plant Materials \(14C\)](#)

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Radiocarbon Dating of Terrestrial Carbonates

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Introduction

Terrestrial carbonates encompass a wide range of materials that potentially could be used for radiocarbon (^{14}C) dating. Biogenic carbonates, including shells and tests of terrestrial and aquatic gastropods, bivalves, ostracodes, and foraminifera, are preserved in a variety of late Quaternary deposits and may be suitable for ^{14}C dating. Primary calcareous deposits (marls, tufa, speleothems) and secondary carbonates (rhizoliths, fracture fill, soil carbonate) may also be targeted for dating when conditions are favorable. This chapter discusses issues that are commonly encountered in ^{14}C dating of terrestrial carbonates, including isotopic disequilibrium and open-system behavior, as well as methods used to determine the reliability of ages derived from these materials. Recent methodological advancements that may improve the accuracy and precision of ^{14}C ages of terrestrial carbonates are also highlighted.

Dating Terrestrial Carbonates

All materials that yield reliable ^{14}C ages have two common characteristics. First, the initial ^{14}C activity of a material must be in isotopic equilibrium with atmospheric ^{14}C at the time it was alive (for living materials) or precipitated (for nonliving materials). Second, it must behave as a closed system with respect to carbon after death or precipitation; that is, secondary (contaminant) carbon is neither added to nor exchanged with carbon that is original to the material itself. If both of these criteria are met, then the measured ^{14}C activity is a function of only two parameters: the initial ^{14}C activity of the atmosphere and the amount of time elapsed since the death of the organism.

The measured ^{14}C activity and age of the material are related by the familiar decay equation

$$A = A_0 e^{-\lambda t}$$

where A and A_0 are the measured and initial ^{14}C activities of the material, respectively; λ is the decay constant of ^{14}C ; and t is the time elapsed since death or precipitation. Conventional radiocarbon ages (incorrectly) assume that atmospheric ^{14}C activity is invariant through time ($A_0 = 1$) and are calculated using the Libby half-life for ^{14}C of $5,568 \pm 30$ years (Libby 1955). Radiocarbon ages can be converted to calendar year ages via calibration to account for temporal variations in the ^{14}C activity of the atmosphere that are known to have occurred (Reimer et al. 2013). Calibration also accounts for the differences between the Libby half-life and the Cambridge half-life for ^{14}C of $5,730 \pm 40$ years (Godwin 1962). If the equilibrium and closed-system

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behavior criteria are met, and the calibration curves are accurate, then the calibrated age of a material should represent its true age in calendar years.

Isotopic Equilibrium

Organisms obtain carbon to build their shells or tests from up to four different sources: air, water, food, and rocks. The ^{14}C activity of these sources ranges from modern (atmospheric CO_2 , live plants, modern water) to ^{14}C -deficient (organic detritus, “old” water) to ^{14}C -free or “dead” (carbonate rocks, coal, some peat deposits). The influence that each of these sources has on the overall ^{14}C content of a shell or test depends on the relative proportion that they contributes to the total carbon pool. For example, if a gastropod obtains all of its shell carbon from air, live plants, and modern water, then the isotopic equilibrium criterion is satisfied and its shell may be suitable for ^{14}C dating. However, if the same gastropod consumed old organic detritus or peat, drank water that was deficient in ^{14}C , or ingested limestone and incorporated the dead carbon in its shell, then the isotopic equilibrium criterion would be violated and the resulting shell age would be too old. Common causes of isotopic disequilibrium in biogenic carbonates are discussed below in order to demonstrate the importance of identifying and quantifying the various sources that contribute carbon to the dated material.

Terrestrial Gastropods and the “Limestone Problem”

Terrestrial gastropods acquire carbon to build their shells from air, water, plants (live and decayed), and carbonate rocks (limestone, dolomite, soil carbonate). Respired CO_2 from the atmosphere is introduced to the bicarbonate pool in the gastropod’s hemolymph and passed along to the extrapallial fluid, from which the shell carbonate is ultimately precipitated (Wilbur 1972). Carbon from food sources (e.g., living plants, fungi, organic detritus) and water (dissolved inorganic carbon; DIC) is also incorporated into the extrapallial fluid and incorporated into the shell material (Balakrishnan and Yapp 2004). Estimates of the individual contributions of atmospheric CO_2 , plants, and water toward gastropod shell carbon vary considerably, but together, in the absence of limestone or carbonate rocks, they account for 100 % of the total input (Goodfriend and Hood 1983; Stott 2002; Romaniello et al. 2008).

In most environments, the ^{14}C activities of live plants and water sources are in equilibrium with atmospheric carbon, which is ideal for ^{14}C dating. However, gastropods also consume organic detritus (i.e., decaying plant litter), which potentially could cause their ^{14}C ages to be anomalously old. In most cases, however, the amount of time elapsed between the death of a plant, its incorporation into decomposition products, and consumption by gastropods is usually quite short, on the order of a few years, which would not affect the resulting ^{14}C ages significantly. Gastropods living in or around coal seams and peatlands are an exception, as they may have access to carbon that is hundreds or even thousands of years old. Similarly, gastropods living in areas of active volcanism, where ^{14}C -deficient carbon in plants may be present, can also yield ages that are much too old. Shell ages derived from gastropods living in these unusual settings should be evaluated carefully.

These exceptions aside, the primary concern with dating terrestrial gastropod shells is the “limestone problem.” A term coined by Goodfriend and Stipp (1983), the limestone problem refers to the fact that many gastropods scrape or abrade carbonate rocks and ingest the powder or granules which then dissolve in their stomach acid to produce CO_2 . As with carbon from other sources, the dead carbon from rocks is introduced to the hemolymph, passed on to the extrapallial fluid, and ultimately incorporated in the shell carbonate. Dead carbon from limestone can account for up to ~30 % of the total carbon in shells of some large terrestrial gastropods, which would cause apparent

^{14}C ages of the shell carbonate to be $\sim 3,000$ ^{14}C years too old (Tamers 1970; Goodfriend and Stipp 1983; Zhou et al. 1999; Pigati et al. 2004). Unfortunately, a simple correction factor that accounts for the limestone effect cannot be applied universally because the amount of old carbon incorporated by gastropods is highly variable, both between taxa and between populations of a single taxon living in different habitats (Goodfriend et al. 1999; Pigati et al. 2010). Thus, to be confident in ^{14}C ages derived from terrestrial gastropod shells, researchers should avoid dating gastropods that incorporate dead carbon from rocks altogether.

Aquatic Organisms and Hard-Water (or Reservoir) Effects

The ^{14}C activity of dissolved inorganic carbon (DIC) in springs and lakes can be lower than atmospheric values for two reasons: (1) interaction between ground water and carbonate rocks, and (2) isotopic decay of DIC that occurs as water molecules travel between areas of recharge and discharge. The magnitude of the local “hard-water” or “reservoir” effect can be highly variable, ranging from negligible to extreme. For water bodies that freely exchange carbon with the atmosphere, the ^{14}C activity of DIC should be in isotopic equilibrium with atmospheric carbon. On the other hand, the ^{14}C activity of ground water flowing through large carbonate aquifers can be very depleted, reaching values as low as $\sim 2\text{--}3\%$ of modern values (e.g., Winograd and Pearson 1976; Riggs 1984). Fully aquatic organisms, such as gill-breathing aquatic gastropods (subclass Prosobranchia), ostracodes, and foraminifera, acquire all of their carbon from aqueous sources, either directly from the water or indirectly from aquatic plants. Thus, the full magnitude of the local hard-water effect is passed on to shells or tests of these organisms. Lung-breathing aquatic and semiaquatic gastropods (subclass Pulmonata) obtain their shell carbon from both water and air and, therefore, are subject to partial hard-water effects. For these gastropods, the offset between true and apparent ages depends on both the magnitude of the local hard-water effect and the proportion of shell carbon derived from aqueous sources and the atmosphere.

Closed-System Behavior

Even if organisms avoid the limestone problem and hard-water effects, their shells or tests must remain closed systems with respect to carbon after death if they are to yield reliable ^{14}C ages. To do so, carbon atoms measured during the ^{14}C dating process must consist solely of those that originally resided in the shell or test. Biogenic carbonates that exhibit open-system behavior typically yield ^{14}C ages that are too young, and the magnitude of the error depends upon the degree of such behavior. Unlike limestone or hard-water effects, which result in discrepancies between measured and actual ^{14}C ages that remain constant over time, the impact of open-system behavior increases with sample age (Fig. 1). For example, if a gastropod shell that is 10,000 ^{14}C years old is contaminated by the equivalent of 1 % modern carbon, then the resulting age would be 9,730 ^{14}C years, a difference of only 270 ^{14}C years. In contrast, if a shell that is 50,000 ^{14}C years old is contaminated by modern carbon to the same extent, the apparent age would be only 35,540 ^{14}C years, a difference of 14,460 ^{14}C years!

Reliable or Not? Evaluating Carbonates for Potential Use in ^{14}C Dating

If terrestrial carbonates are to be used for ^{14}C dating, it is critical that they are evaluated repeatedly in different depositional settings, habitats, and climate regimes to determine if they meet the isotopic equilibrium criterion and behave as closed systems with respect to carbon during burial. Evaluations can be done using at least three different methods: (1) evaluating the ^{14}C content of

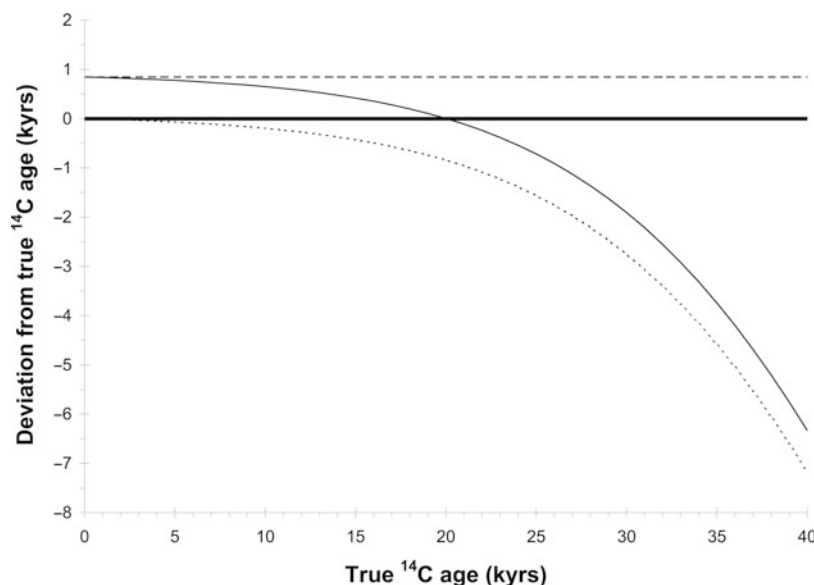


Fig. 1 Deviation from the true ^{14}C age for four scenarios: (1) closed-system behavior and no dead carbon (*thick solid line*), (2) closed-system behavior and 10 % dead carbon (*dashed line*), (3) open-system behavior equivalent to 1 % modern carbon contamination and 10 % dead carbon (*thin solid line*), and (4) open-system behavior equivalent to 1 % modern carbon contamination and no dead carbon (*dotted line*) (After Pigati et al. 2010)

modern specimens, (2) comparing ^{14}C ages of terrestrial carbonates with independent ages, and (3) analytical assessments.

Evaluating Modern Specimens

Evaluating modern specimens for the presence of old carbon from either limestone or hard water can be done with relative ease and minimal cost. Moreover, such evaluations provide worst-case scenarios because the influence of old carbon is most apparent in young/modern samples. In modern evaluations, the ^{14}C activities of live-collected specimens are measured by accelerator mass spectrometry (AMS) and compared against atmospheric values (Hua and Barbetti 2004). If old carbon from limestone or hard water is present, then the measured ^{14}C activity will be lower than the atmosphere. It is critical to perform such evaluations on the specific taxon of interest. For example, Goodfriend and coworkers found evidence of significant (10–30 %) old carbon in large (1–2 cm diameter) gastropods collected live in Texas and elsewhere in the southwestern United States (Goodfriend 1987; Goodfriend et al. 1999). In contrast, Pigati et al. (2004, 2010) examined the ^{14}C activities of small (<1 cm diameter) terrestrial gastropods collected live from limestone or carbonate terrains throughout North America. They found that nearly 80 % of the taxa analyzed did not show evidence of measurable limestone effects. Results from these studies show the importance of evaluating the specific taxon of interest rather than extrapolating results across taxonomic lineages.

Obviously, evaluating modern specimens is only possible if the taxa of interest are still living today, which is not always the case. Moreover, although modern evaluations usually give clear indication of whether old carbon is a problem in the material to be dated, researchers must assume that the results observed remain invariant over time. In general, this appears to be the case for terrestrial gastropods. Terrestrial taxa such as Succineidae, *Discus*, and a few other common small gastropods that appear to avoid limestone in modern settings also yield ages that are similar to independent ages in the fossil record (Pigati et al. 2013). Similarly, *Mesodon* shells are offset from

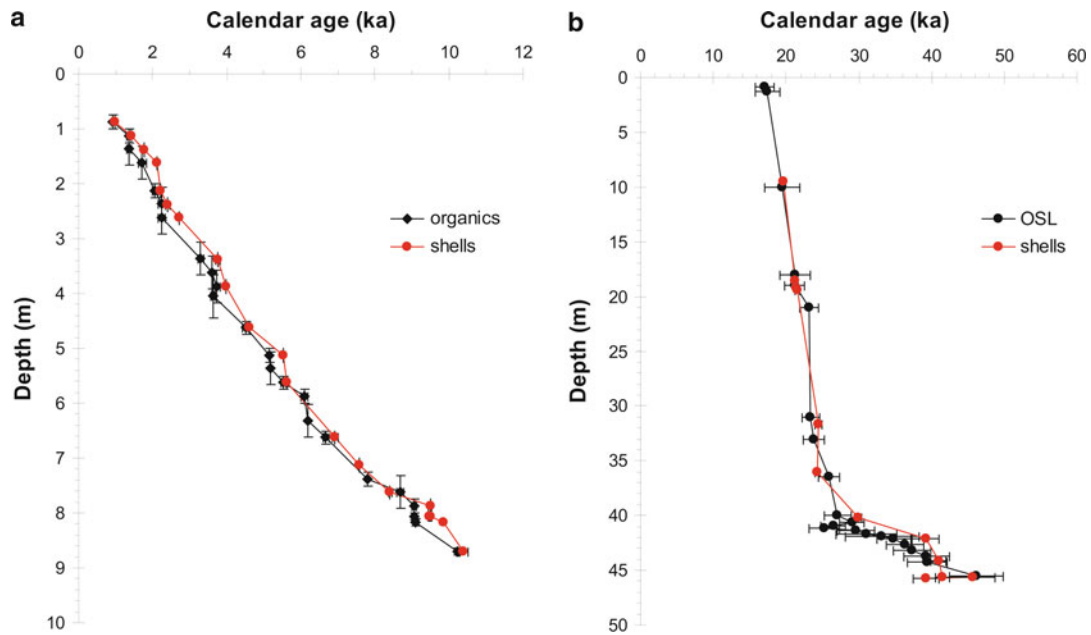


Fig. 2 (a) Independent and gastropod shell ages from a Holocene loess section in Wrangell-St. Elias National Park near Chitina, AK (Muhs et al. 2013b; Pigati et al. 2013). The independent ages consist of calibrated ^{14}C ages from well-preserved wood, and the shell ages are from Succineidae. (b) Independent and gastropod shell ages from loess deposits at Loveland, IA (Muhs et al. 2013a; Pigati et al. 2013). The independent ages consist of optically stimulated luminescence (OSL) ages, and the shell ages are from Succineidae

independent ages by the equivalent of $\sim 3,000$ ^{14}C years or more in both modern systems and the fossil record (Rakovan et al. 2013).

In aquatic environments, researchers can evaluate modern aquatic or semiaquatic organisms living near extant springs and lakes to determine the influence of potential hard-water effects, which are also assumed to be invariant over time. However, hard-water or reservoir effects in some hydrologic systems (mostly lakes) can vary significantly over time because of changes in the balance between hydrologic inputs, say, for example, between runoff and ground water. Thus, if there is reason to believe that the relative contributions of different inputs have varied in the past, then the results of modern evaluations may not be directly applicable to aquatic systems in the geologic record.

Comparison Against Known Ages

One of the best – and most difficult – evaluations to conduct is to compare terrestrial carbonate ages against independent ages to determine if the shells or tests remained closed systems after death. If the evaluations can be conducted for the same time period and environmental conditions represented in the geologic record of interest, then we can be reasonably confident in the results. However, establishing strong independent chronologies is often difficult and costly.

Thus far, there have been relatively few studies conducted in which terrestrial gastropod shell ages have been systematically compared against robust independent ages. Results from loess deposits in Alaska and the Great Plains demonstrate that shell ages (mostly from Succineidae) closely track independent ^{14}C ages derived from plant macrofossils and luminescence ages over the past 40,000 year or so (Fig. 2). Shell ages of terrestrial gastropods from soils and wetland deposits in the southwestern United States and Europe, as well as glacial deposits in the Midwest United States, are also indistinguishable from independent ages, which suggests that many small terrestrial

gastropod shells do, in fact, yield reliable ^{14}C ages for the fossil record, regardless of the local rock type, depositional setting, or climate regime (e.g., Preece 1991, 1994; Pigati et al. 2010, 2011).

Chronologies based on ^{14}C dating of aquatic carbonates can be compared to ^{14}C ages of vascular plant material or charcoal, as well as independently dated chronometric markers such as tephra layers, unique geochemical signatures (e.g., presence of industrialization by-products, anthropogenic indicators), or geomagnetic excursions. In ideal situations, researchers working in aquatic systems should use multiple tie points between the carbonates and independent ages to determine whether the local hard-water effect remained constant over time.

Analytical Assessments

Analytical tools, including scanning electron microscopy (SEM) images and X-ray diffraction (XRD), can be used to determine the nature and physical location of contaminants in terrestrial gastropod shells (Yates 1986; Rech et al. 2011). SEM images can show the position and physical structure of potential contaminants, especially if they are present on the surface of the material dated. However, if chemical exchange has occurred without concomitant morphologic alteration, then SEM imagery may not reveal the contaminants. XRD methods can detect the presence of calcite contaminants in aragonitic shell material, but in most cases the amount of calcite contamination must be at least ~1 % of the total to be detected reliably. If SEM or XRD techniques cannot be applied, then, at a minimum, the shells or tests of terrestrial and aquatic organisms should be broken and inspected under magnification to ensure that they are free of detritus before processing.

Methodologic Innovations

One of the primary assumptions in radiocarbon dating is that the carbon atoms isolated for dating consist solely of atoms that are original to the material itself (i.e., no contamination). Some terrestrial carbonates, such as ostracodes, have exceptionally high surface area-to-volume (SA/V) ratios, which increases the likelihood of chemical exchange with the atmosphere during pretreatment. Standard laboratory procedures for dating carbonate shells or tests often include etching the surfaces with dilute acid, which removes dust and other particulate contaminants. However, recent studies have shown that modern atmospheric carbon can be incorporated into ostracode tests by either surface adsorption or exchange during laboratory processing (Hajdas et al. 2004). Such contamination may not necessarily be removed during the etching process. Stepped-dissolution experiments using ostracode tests show that even after etching, younger carbon is preferentially released during initial acid dissolution steps (i.e., contaminants plus sample material), whereas older carbon is released in later steps, presumably all original to the sample (Zimmerman et al. 2012). These results imply that if the SA/V ratio of a material is high enough, contaminants can be missed by standard laboratory pretreatment protocols and the resulting ^{14}C ages would be too young. Although stepped-dissolution procedures can be time consuming, technically challenging, and expensive if multiple aliquots are measured by AMS, they may ultimately yield ^{14}C ages that are more accurate and precise than those obtained using standard methods.

Conclusions

Terrestrial carbonates encompass a wide variety of materials that can potentially be used for ^{14}C dating. However, issues related to isotopic disequilibrium and open-system behavior must be addressed before ^{14}C ages derived from these materials are considered reliable. Removing contaminating materials from terrestrial carbonates can be difficult because the contaminant species is often calcite, which may be the same as, or similar to, the sample material. For biogenic carbonates that are composed of aragonite, small amounts of calcite contamination may be detected using scanning electron microscopy or X-ray diffraction. In the fossil record, ^{14}C ages derived from terrestrial carbonates should be compared against ^{14}C ages of independent materials (ideally charcoal or plant macrofossils) in depositional settings and time periods that are similar to those in the geologic record of interest. If the terrestrial carbonates consistently meet the isotopic equilibrium and closed-system behavior criteria, then the materials should yield reliable ^{14}C ages. New methodological and technological innovations may improve the accuracy and precision of ^{14}C ages of terrestrial carbonates, which is particularly important as high-resolution chronologies are increasingly given high priority in paleoclimate and other studies.

Acknowledgments

This manuscript benefited from constructive reviews from Gene Ellis, Dan Muhs, and Tim Jull. This project was funded by the U.S. Geological Survey Climate and Land Use Change Research and Development Program.

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Corals (Sclerochronology)

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Synonyms

[Coral chronometer](#); [Related to dendrochronology](#)

Definition

Sclerochronology: The study of the incremental layers contained in the hard parts or skeletons of organisms that form at regular intervals during the organism's life span. Sclerochronology is derived from the Greek words *sklero* meaning "hard," *khronos* meaning "time," and *logos* meaning "science of." Sclerochronology is related to dendrochronology or the study of annual growth rings in trees.

Coral: Corals are in the class Anthozoa of the phylum Cnidaria and include scleractinian or "stony corals," which form colonies of many individual polyps with an external skeleton or exoskeleton of calcium carbonate (CaCO_3), and non-stony corals or soft corals. Some stony corals contain incremental layers in their exoskeleton. Coral-based sclerochronological research is focused on stony corals yet recent research reveals that some soft coral species contain incremental layers (see Roark et al. [2006](#)).

Introduction

The general term of sclerochronology includes a diverse array of marine and terrestrial organisms, both extinct and extant, that produce hard structures with regular time intervals related to the organism's growth and/or environment. Such organisms include corals, molluscs, fish otoliths or "ear bones," coralline algae, sclerosponges, brachiopods, and bones of vertebrate animals with research expanding to other organisms (see Arnold and Jones [2007](#); Schöne [2010](#)). This description is focused on coral-based sclerochronology, in particular scleractinian corals, with descriptions of mollusc-based sclerochronology appearing in another entry.

The exoskeleton of scleractinian corals is composed of aragonite, a mineral form of calcium carbonate, deposited by the living coral polyps within the surface of the exoskeleton. The individual coral polyps calcify new skeleton thecal "walls" and dissepiment "floors," lifting up as new skeleton is created, similar to building a skyscraper. As the coral deposits its skeleton, it produces a high-density band and a low-density band each year while simultaneously recording environmental signals, such as water temperature and chemistry, in its skeleton (e.g., $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and Sr/Ca). Coral colonies have different morphologies including branching, columnar, and

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boulder-shaped or massive corals, for which annual density bands are found in massive and columnar colonies. Massive coral colonies, which grow up to 8 m in height (Veron 1986; Isdale et al. 1998; Corrège 2006; Brown et al. 2009), can live for many centuries providing a continuous annual chronology preserved in its exoskeleton. Coral sclerochronology is used for establishing time for a variety of purposes including paleoceanographic and paleoclimatic reconstructions, investigations of environmental change, refining radiometric dating methods, assessing sea-level variations, and documenting earthquakes.

History

Research on coral reefs began in earnest with Charles Darwin's hypothesis of reef formation with the passage of time (Darwin 1842). Early work with the branching coral *Acropora palmata* in the Bahamas notes regular undulations on the surface of the broad fronds (Whitfield 1898) shown empirically as annual in nature (Vaughan 1915). A Chinese paleontologist, Ting-Ying H. Ma (1934), notes that Paleozoic and recent corals contain internal skeletal structures with varying densities. The report of Wells (1963) examines diurnal growth lines in the epitheca of Devonian corals, which he interprets as evidence for more days in a Devonian year compared to present.

Despite these early studies, the annual nature of density variations within coral skeletons is not confirmed until the study of Knutson et al. (1972) examines corals from the nuclear test site at Eniwetok Atoll. That study uses autoradiography to image radioactive layers in the coral colony by placing X-ray film in contact with a thin radial cross section for over one month. Next, they couple autoradiography with X-radiography, which reveals alternating high- and low-density bands in the cross section, and then count the number of density band couplets between the radioactive bands. They found the number of bands equals the number of years between nuclear weapons tests, thus confirming the annual nature of high-low-density bands in corals. Knutson et al. (1972) suggest combining the “coral internal calendar” with isotope thermometry in corals (Weber and Woodhead 1972) will allow for the “construction of coral-ring chronologies” of past oceanic variability, similar to dendrochronology. In June 1973, the papers presented at the Second International Symposium on Coral Reefs include publications related to sclerochronology (Buddemeier 1974; Macintyre and Smith 1974; Moore and Krishnaswami 1974). The use of term “sclerochronology” first appears in two 1974 publications (Buddemeier et al. 1974; Macintyre and Smith 1974), yet this term appears to originate from this conference. Subsequent studies confirm the annual nature of the density couplets for Atlantic and Indo-Pacific coral species by radiometric analysis, staining, and direct measurement (Buddemeier 1974; Buddemeier et al. 1974; Dodge and Thomson 1974; Macintyre and Smith 1974; Moore and Krishnaswami 1974) as well as revealing diurnal increments (Barnes 1970) and monthly or lunar cycles (Buddemeier 1974).

Sclerochronological Methods

Samples for sclerochronological studies include cores, 3–10 cm in diameter, extracted from large colonies using hydraulic or pneumatic drills or whole colonies if small enough to recover by divers or by a boat-mounted winch. The cores or colonies are sectioned along the primary growth axis to thin slabs of constant thickness of approximately 0.5 cm. The slabs are exposed to X-rays to produce X-radiographs (i.e., X-ray images) using either film or digital X-ray systems. X-radiographs are negative images exhibiting density variations from light high-density areas to

dark low-density areas in the coral slab for which alternating bands of high and low density represent a single year's growth. Years are assigned by counting annual density couplets from a known date or collection date from the top of the slab following the density bands and growth patterns. A floating chronology (e.g., year 1, year 2, etc.) is utilized for samples without a known collection date such as dead or fossil corals.

Two parameters of coral growth are measured from X-radiographs: linear extension per year (cm/year) and skeletal density (g/cm^3), both of which vary independently on a seasonal basis. Relative calcification rate ($\text{g}/\text{cm}^3/\text{year}$) is the product of linear extension and density. Annual linear extension (cm) is physically measured from the top of one high-density band to the top of the next high-density band using calipers. X-ray and gamma densitometers provide density measurements from coral slabs (Buddemeier 1974; Dodge and Thomson 1974; Chalker et al. 1985; Chalker and Barnes 1990). For digital X-radiographs, imaging software such as Coral XDS (www.nova.edu/ocean/coralxds) (Helmle et al. 2002), Image J (sb.info.nih.gov/ij), and Adobe Photoshop[®] (www.photoshop.com) are used to determine linear extension and relative density. Linear extension can be determined from the winter extremes in seasonal coral chemical variations (e.g., $\delta^{18}\text{O}$ or Sr/Ca) using the distance (i.e., cm from core top) between these samples. This method is particularly useful for comparing chemical variations and extension rates, but precision is limited to the chemical sampling resolution.

The study of Dodge and Thomson (1974) is the first to apply methodologies from dendrochronology to build a master chronology using density variations from multiple coral colonies in Bermuda. Further work with a larger network of colonies reveals long-term covariance with temperature and air pressure records (Dodge and Vaisnys 1975). The report of Hudson et al. (1976) demonstrates that stress bands in *Montastraea annularis* formed by cold events can be used as stratigraphic markers for cross-dating between live and dead colonies from the same reef. Some corals skeletons contain luminescent lines under ultra-violet light from soil-derived humic acids that are interpreted as proxies of coastal precipitation and runoff (Boto and Isdale 1985; Omata et al. 2006; Grove et al. 2010). Researchers utilize these lines to cross-date coral colonies to produce runoff histories for individual rivers and regional scale precipitation reconstructions that span multiple centuries (Isdale et al. 1998; Hendy et al. 2003; Nyberg et al. 2007; Lough 2011). Cross-dated luminescence corals are coupled with chemical records to extend these records back in time (Tudhope et al. 1996; Hendy et al. 2002). The study of Cobb et al. (2003) uses high-precision uranium-thorium dating (± 5 –10 years) and correlation between coral $\delta^{18}\text{O}$ variations to generate long overlapping coral records reconstructing El Niño-Southern Oscillation variability (Cobb et al. 2013). A relatively new application is cross-dating coral Sr/Ca variations, a temperature proxy, between cores from the same *Porites lutea* colony to produce a 350-year-long sea surface temperature (SST) reconstruction (DeLong et al. 2012). Those authors confirm their cross-dated Sr/Ca chronology with high-precision (± 1 year) ^{230}Th dating (Shen et al. 2008), which allows them to assess sources of chronology error (DeLong et al. 2013). Further application of this cross-dating method with live and dead *Siderastrea siderea* corals has produced a 274-year-long SST reconstruction for the Gulf of Mexico (DeLong et al. [In Review](#)).

Applications of Coral Sclerochronology

Growth in corals varies with environmental factors such as temperature, light, and nutrients; thus, environmental variations are recorded in the sclerochronology. Initial studies at Eniwetok suggest that density bands in the corals form in response to seasonal variations in cloud cover or

precipitation (Knutson et al. 1972; Buddemeier et al. 1974). Conversely, the report of Weber et al. (1975), with a wide array of corals in locality and genera, finds seasonal temperature variations drive coral growth rates. Further research with coral growth records continues to produce conflicting results (see reviews of Buddemeier and Kinzie 1976; Barnes and Lough 1996); consequently, these records were relegated to chronology development for coral chemical studies in the early 1990s, yet recent interest in ocean acidification has revived interest in coral growth histories (see reviews of Lough 2008; Lough and Cooper 2011).

Soon after the confirmation of annual increments in corals, researchers started sampling coral skeletons across the density bands to produce time series of chemical variability. These early studies coupled sclerochronology with coral chemistry including stable isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) (Goreau 1977; Emiliani et al. 1978; Nozaki et al. 1978; Fairbanks and Dodge 1979), trace elements (Fe, Mg, Na, and Sr) (Goreau 1977; Oomori et al. 1982; Schneider and Smith 1982), and radiocarbon (Druffel 1980). These coral chemical variations and others represent water chemistry histories (e.g., B, Ba/Ca, ^{14}C , Mn/Ca, P/Ca, and Pb/Ca) as well as serve as proxies for water temperature ($\delta^{18}\text{O}$, Mg/Ca, Sr/Ca, and U/Ca) and ocean circulation (e.g., ^{14}C , Ba, and Cd) (see reviews of Shen 1993; Druffel 1997). Advances in sampling methodologies (e.g., up to weekly) and analytical improvements (i.e., reducing the amount of sample needed and improved analytical precision) have resulted in rapidly expanding coral chemical research compared to growth-rate studies (Lough and Cooper 2011). Coral sclerochronology-chemistry studies include numerous high-resolution, multi-century long records (see www.ncdc.noaa.gov/paleo/corals) that provide valuable information to the fields of paleoclimatology, ocean circulation, and environmental change (see reviews of Swart 1983; Druffel 1997; Gagan et al. 2000; Cole 2003; Felis and Patzold 2004; Corrège 2006; Grottoli and Eakin 2007; Lough 2010).

The sclerochronology determined by counting the annual bands in corals allows for comparisons with radiometric dating methods (e.g., U-Th) to improve analytical methods (e.g., Shen et al. 2008, 2012; Clark et al. 2012). Radioisotopes are incorporated in the coral exoskeleton during calcification (e.g., ^{14}C , ^{228}Ra , and ^{210}Pb) or by decay after incorporation (e.g., ^{230}Th and ^{231}Pa). Uranium-thorium (U-Th) dating of carbonates provides ages with high precision (± 3 years) with relatively small sample sizes (Edwards et al. 1987). The study of Shen et al. (2008) refines U-Th dating for corals by measuring 141 coral samples each extracted from a single density band of known age, determined by counting annual bands. Those authors demonstrate that corals with an age less than 100 years can be ^{230}Th -dated with a precision of ± 1 year. Further analytical refinement resulted in reduced sample size for U-Th analysis (10–50 mg of coral carbonate) with a precision of less than ± 1 year (Shen et al. 2012). Such high-precision U-Th dates allow for the cross-dating of dead and fossil corals to extend the inclusive records further in time (e.g., DeLong et al. In Review).

Microatolls are massive corals in very shallow water with a dead flat or concave top resembling an atoll island. As these corals grow out of the water, the exposed surface dies while the submerge surface continues to live; thus, these corals serve as an indicator of sea level (Smithers and Woodroffe 2000). Counting the annual bands in the coral's X-radiograph reveals the date the coral surface emerged from the water. Using microatolls as tide gauges, the study of Taylor et al. (1987) documents the date of four earthquake events in Vanuatu, an island in the southwest Pacific, that uplifted the corals during earthquakes. These coral earthquake records provide dates of past earthquakes in remote areas that lack such records, as well as information on vertical uplifting rates and seismic movements (Buskirk et al. 1982; Taylor et al. 1982). Other researchers utilize microatolls to study twentieth-century sea-level variations (e.g., Smithers and Woodroffe 2001) and Holocene sea-level changes (e.g., Yu et al. 2009; Woodroffe et al. 2012). Investigations with

microatolls include corals from the tropical Pacific, Indian, and Atlantic oceans (see review of Buddemeier and Taylor 2000).

Summary

Coral sclerochronology started with the discovery of annual density bands within the coral skeleton. These bands are visible in X-radiographs and dates are assigned by counting bands from the collection date. The primary use of coral sclerochronology is assigning time to synchronous chemical records store in the skeletons of these long-lived organisms. These time series of coral chemical variations are used for paleoclimate reconstructions, investigations of environmental change, and refining radiometric dating methods. Additionally, annual density bands in corals are utilized to investigate changes in sea level and earthquakes. The field of coral sclerochronology is continually advancing with new applications being developed to decipher the hidden messages stored in the skeletons of corals.

Cross-References

- ▶ [Dendrochronology, Palaeoclimate](#)
- ▶ [Luminescence, Biogenic Carbonates](#)
- ▶ [Luminescence, Coastal Sediments](#)
- ▶ [Sclerochronology, Bivalves](#)
- ▶ [Uranium Series, Palaeoclimate](#)
- ▶ [Uranium Series, Sea-level Change](#)

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Glacial Landscape (Cosmogenic Nuclide)

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Introduction

Cosmogenic nuclides have become powerful tools to explore glacial landscapes toward reconstructing cryospheric change (Balco 2011) on a wide spectrum of time scales and are currently revolutionizing the fields of glacial geology, terrestrial climate, cryosphere science, and earth surface process geomorphology. Whenever glaciers and ice sheets fluctuate, the mighty ice alters the earth surface, carves previously unexposed surfaces, and deposits glacial sediments, including moraine ridges. Exposure of such newly formed glacial surfaces to the cosmic radiation at the moment of ice retreat starts the cosmogenic nuclide clock (referred to as “► [Cosmogenic Nuclide Dating](#)”; See also “► [Cosmogenic Nuclide](#)” overview entry in the same issue and the following seminal review articles: Cerling and Craig (1994), Gosse and Phillips (2001), Granger et al. (2013), Lal (1991)). About 20 years ago, pioneering studies first applied cosmogenic nuclide techniques to date moraines, glacially formed ridges of rock and soil that mark former glacier positions (e.g., Brook et al. 1993; Gosse et al. 1995; Ivy-Ochs et al. 1999). Since then, originally paced by progress by John Stone (University of Washington, Seattle), the sensitivity of cosmogenic nuclide techniques has been transformationally refined (e.g., Stone et al. 2003). Also, new cosmogenic nuclide tools, further widening the application spectrum, have been introduced, most recently the “in situ ^{14}C ” technique, developed and implemented by Nat Lifton (Lifton et al. 2001). Time scales to cosmogenically clock land ice change now span from many million years (Bruno et al. 1997; Ivy-Ochs et al. 1997; Margerison et al. 2005; Schäfer et al. 1999) to 100 years ago and less (Kelly et al. 2008; Licciardi et al. 2009; Schaefer et al. 2009; Schimmelpfennig et al. 2014; Stroup et al. 2014). Novel cosmogenic nuclide applications include dating of the first maximum of the Laurentide Ice Sheet (Balco et al. 2005) using buried tills in the central USA and constraining past ice sheet fluctuations in Antarctica by cosmogenic nuclide dating of “nunatak dipsticks,” ice-free rock formations towering above the ice sheet (Balco et al. 2013; Johnson et al. 2014). Other recent studies pioneer the application of cosmogenic nuclide techniques to explore pro- and subglacial bedrock as environmental archive (Goehring et al. 2013, 2011). All these successes are the product of an integrated science approach, crosscutting the disciplines of Quaternary Geology (geomorphic mapping), Glaciology (glacier dynamics), Geochemistry (cosmogenic nuclide analysis), and Climate Science (synthesis). This short entry attempts to illustrate the breathtaking dynamic of progress in cosmogenic nuclide science by presenting application examples toward forefront questions in climate and glacier science. Here, we primarily focus on the cosmogenic nuclide ^{10}Be . Other cosmogenic nuclide techniques, in particular ^3He (Blard et al. 2013b; Goehring et al. 2010; Kurz 1986), ^{36}Cl (Schimmelpfennig 2009; Schimmelpfennig et al. 2011), and in situ ^{14}C (Goehring et al. 2014; Hippe et al. 2014, 2013; Lifton et al. 2001), are rapidly progressing, but covering all cosmogenic nuclides would be beyond scope and space of this entry.

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Methods

Cosmogenic Nuclide Production Rates

Here, we review recent progress in our quantitative understanding of cosmogenic nuclide production rates. For a detailed methodological overview, see the accompanying entry “► [Cosmogenic Nuclide](#)” (REF) and references therein. Cosmogenic nuclide surface exposure dating is based on the measurement of minute amounts of cosmogenic nuclides, here ^{10}Be , produced in near-surface rocks as a function of time, after glacier retreat has exposed the “new” surface to cosmogenic radiation (time = zero of the cosmogenic clock). By careful sample selection in the field, we minimize secondary influences, compromising this approach, such as inheritance of cosmogenic nuclides in the sampled surface from prior periods of exposure, temporary shielding of the sampled surface by snow or sediment cover, or considerably erosion of the surface. These potentially compromising influences can also be evaluated by measuring many samples of the same glacial feature and thus the same expected cosmogenic nuclide inventory (see below).

To calculate a “surface exposure age” from the measured ^{10}Be concentration in the surface sample, we need to know the ^{10}Be production rate at the sample location integrated over the full period of exposure. The uncertainty of this production rate value linearly propagates into the overall age error. Because incoming cosmic radiation is shielded by the Earth’s atmosphere and the geomagnetic field, production rates of cosmogenic nuclides at the earth’s surface are a function of altitude, latitude, and time (see accompanying entry “► [Cosmogenic Nuclides](#)”). As an example, the altitudinal scaling factor from sea level to 2,000 is ~ 4.8 .

The uncertainty in the knowledge of the time-integrated production rate at the location of the study has remained the major source of error in cosmogenic nuclide studies. However, there is good news! Over the last few years, several studies have shown the potential to locally calibrate ^{10}Be production rates (and ^3He production rates) with a precision of better than 3 % (1σ) (e.g., Fenton et al. 2011; Kaplan et al. 2011; Putnam et al. 2010; Young et al. 2013). In Fig. 1, we plot a compilation of recent local ^{10}Be production rate calibrations that we believe to be robust, scaled

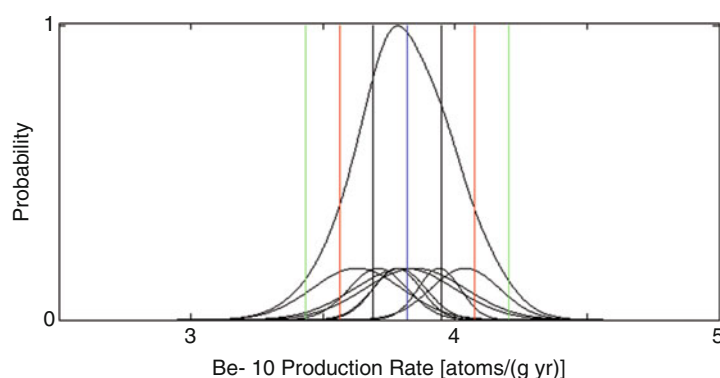


Fig. 1 Consistency of recent ^{10}Be production rate calibrations. Production rate calibration experiments from Norway (Oldedalen Landslide (Goehring et al. 2012a) and Grotlandsura Landslide (Fenton et al. 2011)), Greenland (Young et al. 2013), New England (Balco et al. 2009), tropical Peru (Kelly et al. in press), tropical Bolivia (Blard et al. 2013a), New Zealand (Putnam et al. 2010), and Patagonia (Kaplan et al. 2011) shown by *thin line*, the *bold curve* gives the integrative probability function. The *blue vertical line* is the arithmetic mean, and the *black vertical line* gives the 1σ uncertainties, *red line* the 2σ , and *green line* the 3σ range. Following the convention, all values are scaled to sea level and high latitudes using the time-dependent “Lm” scaling after (Balco et al. 2008) (see also text). This tight cluster of ^{10}Be production rate calibrations has been produced over the last 3 years and reflects the considerable progress relative to the earlier “global ^{10}Be production rate” value of 4.4 ± 0.4 atoms/(g year) (Balco et al. 2008)

for reference to sea level and high latitude using the same scaling scheme (Lal/Stone time-dependent “Lm” after Balco et al. (2008)). The overall picture is one of striking internal consistency, and these experiments afford for high-precision cosmogenic dating studies near the production rate calibration points. Simultaneously, new modeling approaches (Argento et al. 2012; Lifton et al. 2014) to scale between the locations of production rate calibrations improve and converge as well toward the original scaling factors published by Lal in 1991 (Lal 1991). With the current rate of progress of production rate calibrations and model interpolations in between, it appears realistic to project a robust, near-global network of production rate values allowing for precise and accurate cosmogenic dating studies anywhere on earth in the near future.

Novel Applications of Cosmogenic Nuclides to Glacial Landscapes

The First Glacial Maximum in North America

When did the first ice age peak? When did Earth’s climate commence to swing between full glacial and interglacial modes? These long-standing geological questions have been elegantly addressed recently by a series of studies (Balco and Rovey 2008; Balco and Rovey 2010; Balco et al. 2005), dating the lowest, and thus oldest, glacial tills in the central USA by means of cosmogenic $^{26}\text{Al}/^{10}\text{Be}$ burial dating (Balco and Shuster 2009; Granger and Muzikar 2001). The cosmogenic burial dating method makes use of the difference in half-life of two (or more) cosmogenic nuclides in sediments that had have been buried after a period of exposure and thus cosmogenic nuclide production. During the period of burial of sediments, the nuclide with the shorter half-life, here ^{26}Al ($t_{1/2} = 717,000$ years), decays faster than the longer-lived nuclide, here ^{10}Be ($t_{1/2} = 1,400,000$ years). Hence, the measured $^{26}\text{Al}/^{10}\text{Be}$ ratio in buried sediments quantifies the burial time and, in this case, dates the deposition of the oldest glacial tills and the first glacial maximum of the Laurentide Ice Sheet to about 2.42 ± 0.14 million years. This result represents the most robust date for the first maximum of the predominant northern continental ice sheet and postdates the onset of the Quaternary.

The Structure of the Last Glacial Maximum in New Zealand’s Southern Alps

A recent example of a comprehensive, high-sensitivity ^{10}Be chronology from boulders protruding from moraines at Lake Ohau, New Zealand’s Southern Alps, yielding new information about the structure of the Last Glacial Maximum (LGM) in southern mid-latitudes (Putnam et al. 2013b), is shown in Fig. 2. It is the internal consistency of ^{10}Be boulder ages within these multi-sample data sets that best highlights that glacier moraine records are uniquely suitable for the cosmogenic SED approach and that secondary, potentially compromising processes such as snow and sediment cover of the sampled surface, turning of the sample after deposition by the glacier on top of the moraine, and finally inheritance of cosmogenic nuclides in the sample from prior periods of exposure are not significant in well-selected settings.

This chronology shows an extended mountain glacier LGM in New Zealand, with culminations at about 32, 26, 22, and 18 ka ago, and illustrates the potential to reconstruct glacier fluctuations during the last ice age with millennial resolution. Beyond, the ^{10}Be ages on the green moraines in Fig. 2 indicate that in some cases, the SED method can provide age information about the glacier culmination at the end of the penultimate glacial cycle.

From the paleoclimatic perspective, the LGM moraine records from New Zealand add new and robust information about the onset, fine structure, and termination of the Last Glacial Maximum in southern mid-latitude. Because New Zealand’s glaciers respond most sensitively to summer temperatures (Anderson and Mackintosh 2006; Anderson and Mackintosh 2012; Golledge et al. 2012),

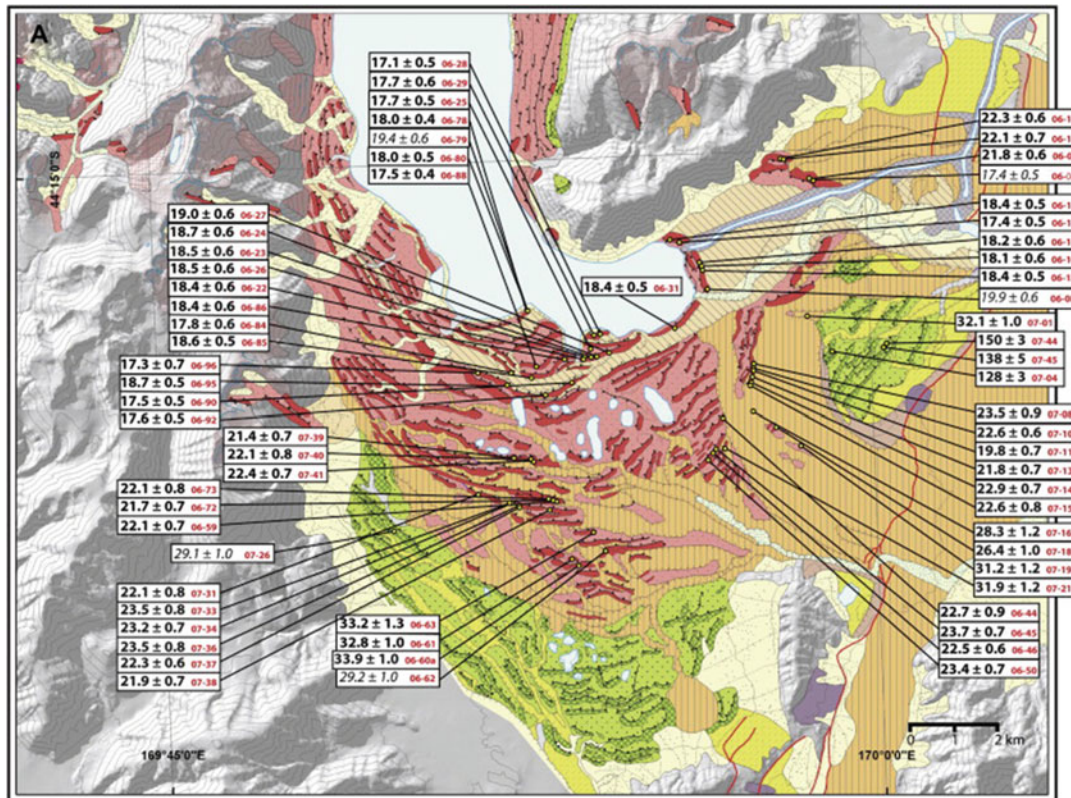


Fig. 2 ^{10}Be boulder chronology for Last Glacial Maximum glacier culminations in New Zealand's Southern Alps (Modified after Putnam et al. (2013b). Red = Last Glacial Maximum (LGM) moraines; green = pre-LGM moraines. Boxes give ^{10}Be ages of boulders on moraines, outliers plotted in italic. Note the high internal consistency of ^{10}Be ages from boulders from one moraine sequence, together with the detailed stratigraphic order of the moraine ages (inboard moraines are younger). The few old ages on the green moraine represent the glacier position at the end of the penultimate ice age, indicating that the SED method can be used over orbital time scales in some cases)

the glacier fluctuations can be transformed into a temperature record, which implies that LGM summers in New Zealand were about 6–7 °C cooler than today. Beyond, the long LGM in New Zealand was punctuated by multiple culminations that show striking similarity to Antarctic ice core temperature records (Fudge et al. 2013) and sea surface temperature records in the southern ocean. This multiple culmination structure of the LGM rules out southern summer insolation as driver of the LGM in New Zealand, because 44°S December insolation was rising steadily through the New Zealand LGM period, from its minimum 32,000 years ago until the insolation peak some 22,000 years ago. Finally, the abrupt termination of the LGM in the moraine record commencing at about 18,000 years ago is a near match to the atmospheric CO_2 curve. Together with the timing of the culmination during the long LGM period, a northern hemisphere driver connected to atmospheric greenhouse gas concentrations appears to be the most promising scenario to explain the southern mid-latitude LGM pattern (Putnam et al. 2013a).

Proglacial Bedrock as Climate Archive: Holocene Fluctuations of Rhone Glacier

Recent studies by Goehring et al. (2011, 2012b) introduce high-sensitivity cosmogenic nuclide techniques as tools to explore the bedrock exposed only a few years ago by Rhone Glacier, Swiss Alps, toward reconstructions of Holocene glacier dynamics. Here, two cosmogenic nuclides produce in quartz, in situ ^{14}C and ^{10}Be , were used in concert to evaluate the periods during which the

Rhone Glacier was smaller or bigger, respectively, than today over the Holocene period (the last 11,500 years). The cosmogenic nuclide concentrations through any glacier forefield decrease from margin to central trough, which is consistent with the erosion profile showing higher erosion rates where the glacier flows faster (center), compared to the slower-flowing margins. We can assume that this bedrock was free of cosmogenic nuclides at the end of the last ice age some 11,500 years ago, after tens of thousands of years of big glaciers and subglacial erosion. In turn, the ^{10}Be ages of the bedrock samples at the margin of the Rhone Glacier trough provide minimum estimates of exposure, so the integrated period of time during which Rhone Glacier was smaller than today over the last 11,500 years. The dual-nuclide approach in this case suggests that Rhone Glacier was smaller than today for about 55% of the Holocene and that the most likely scenario describes a small Rhone Glacier to the early and mid-Holocene, followed by a larger Rhone glacier over the last 4000 years. This cosmogenic nuclide-based scenario, updated toward higher precision in a second isochron-based study (Goehring et al. 2013), agrees well with climate proxy records from the Alps and elsewhere in the northern hemisphere, making the case for warmer-than-today climate during the early and mid-Holocene, followed by climate deterioration and regrowing glaciers around 4,000 years ago, peaking during the Little Ice Age (1300–1850 CE).

Rock Dipsticks to Measure Ice Sheet Fluctuations: Rapid Thinning of the Pine Island Glacier, a Major Outlet Glacier of the West Antarctic Ice Sheet

The West Antarctic Ice Sheet (WAIS) is potentially unstable in our warming world and could contribute up to 3.5 m of sudden sea level rise, which would be a disastrous environmental change. Applying for the first time ^{10}Be techniques to Holocene glacial deposits along an altitude transect (dipstick approach), Stone et al. (Stone et al. 2003) showed that the WAIS has been steadily thinning during the Holocene. On top of the long-term thinning trend, modern observation from the Pine Island Glacier (PIG), one of the major outlet glaciers of the WAIS, shows very rapid thinning at a rate of about 1 m per year over the recent years (Park et al. 2013). The questions whether the current rapid thinning is unique, how sustainable it might be, and what actually drives the PIG thinning are fundamental to WAIS stability and global sea level predictions.

A new study has applied cosmogenic nuclide techniques to a rock dipstick (Fig. 3) above an unnamed outlet glacier directly linked to the PIG. The rock formation towering over the ice sheet and the PIG tributary has been steadily exposed during the ice sheet thinning, and this signal is traceable by high-sensitivity ^{10}Be techniques. The data shown in Fig. 3 illustrates that a rapid thinning of the PIG occurred about 8,000 years ago and lowered the PIG surface over 100 m over about a century. Thus, the thinning rate of the PIG 8,000 year ago was similar to the modern thinning rate but was sustained over 100 years. The most likely explanation for the rapid and sustained PIG thinning 8,000 years ago is a breakup of the Pine Island Bay ice shelves (Fig. 3, upper panel). Such ice shelves buttress the outlet glaciers while intact, and vice versa, if the buttress disappears, the outlet glacier flow accelerates dramatically, thinning the outlet glacier and draining the ice sheet. This happened 8,000 years ago, during a climate period that was not even close to the current greenhouse gas-induced climate forcing. While the comparison between the PIG and WAIS dynamics 8,000 years ago and today is complex, this experiment illustrates the high sensitivity of the PIG and its ice shelves, and thus the WAIS, to climate forcing. This is a worrisome result, given that the warming of our planet accelerates and that transport of warm ocean waters to the Amundsen Sea Embayment (Fig. 3) is one of the observed consequences (Martinson 2012). By this argument, we must expect that current thinning of the PIG continues and might accelerate, which will translate into a rapidly increasing melt water signal coming from the WAIS.

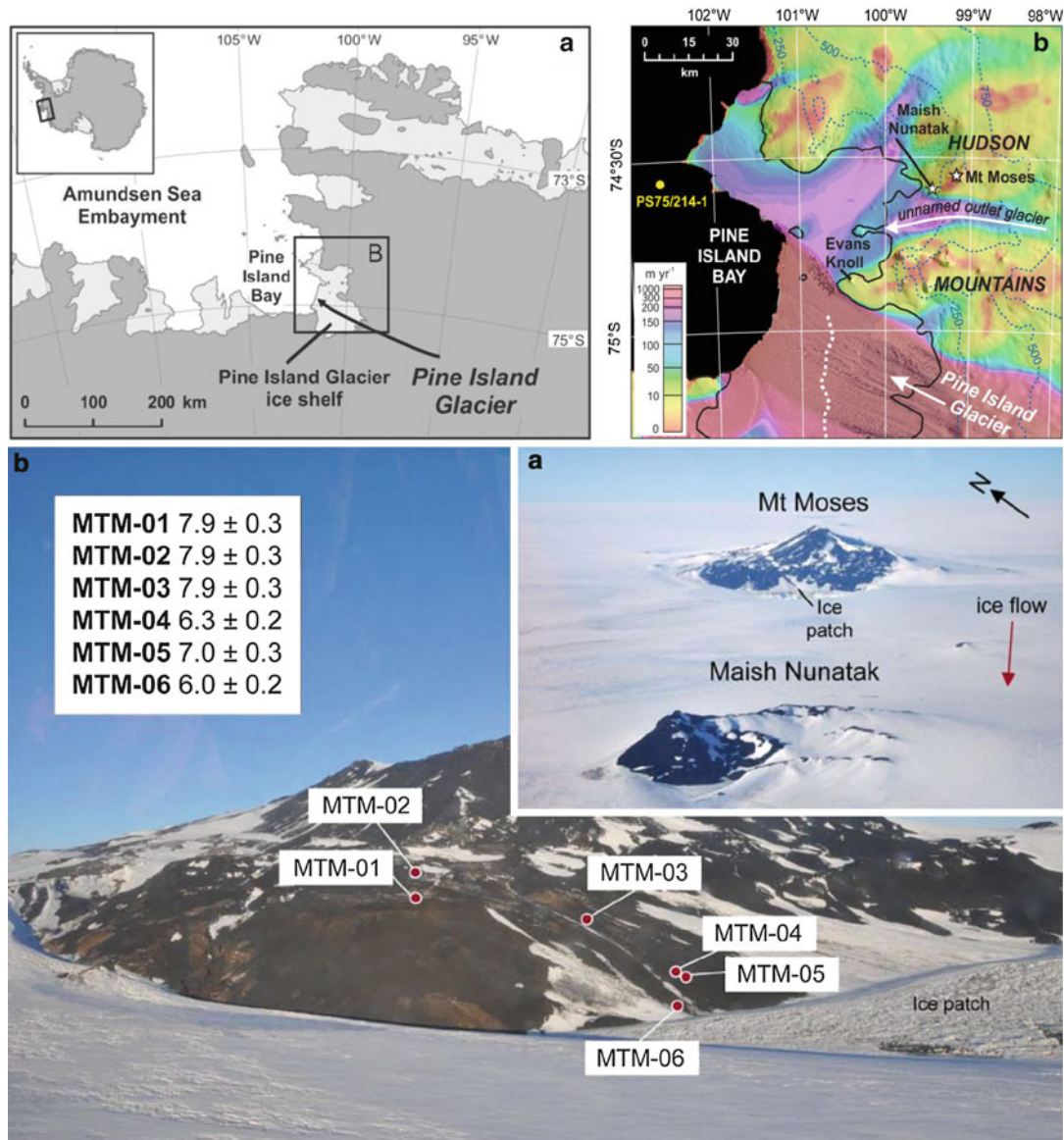


Fig. 3 Rock outcrops as dipsticks of ice sheet thinning (Modified after Johnson et al. [in press](#)). *Upper left panel:* Map of the Amundsen Sea Embayment, showing location of the study area. The grounded ice sheet is shown in *dark gray* and ice shelves in *light gray*. The *inset* shows the location within Antarctica, and the *box* shows the study area. *Upper right panel:* Map of Pine Island Bay, showing flow velocities of Pine Island Glacier and the unnamed outlet glacier flowing through the Hudson Mountains. Contours are in meters. The *grounding line* is represented by the *solid black line*, and the crest of the sub-ice shelf ridge as a *dashed white line*. *Lower panel:* Dipstick rock outcrop towering above the unnamed outlet glacier connected to Pine Island Glacier, West Antarctic Ice Sheet, with sample locations along an altitude transect and ^{10}Be ages shown

Synopsis

Cosmogenic nuclide techniques have revolutionized our capabilities to exploit glacial landscapes toward reconstruction of past land ice change and climate variability. Yet, this might be just the tip of the iceberg. High-sensitivity cosmogenic nuclide techniques applied to the moraine record now afford for precise reconstruction of past glacier fluctuations with centennial resolution and on a time scale ranging from decades to beyond 100,000 years. It has been a long-standing dream of geologists

and climate scientists alike to precisely map land ice change during the last ice age through the deglaciation period and into the current interglacial, referred to as the Holocene. This dream appears now in reach. Of course, there is a tremendous amount of scientific work ahead to realize this dream, but there is no daunting scientific challenge ahead; we simply need to intensify the multidisciplinary efforts toward precise and accurate cosmogenic nuclide studies of glacial landscapes, which depends critically on more cutting-edge cosmogenic production rate calibrations at different latitudes and altitudes and also on funding resources! Beyond the moraine program, it is a central goal to further improve the sensitivity of other cosmogenic nuclide systems, in particular ^3He , ^{36}Cl , and in situ ^{14}C , and to develop the multi-nuclide approaches further. Finally, from the proglacial bedrock studies described above, it appears a natural next step to use subglacial bedrock as climate archive. Subglacial bedrock holds the isotopic answer to fundamental questions such as: When did the WAIS collapse the last time? When was Greenland ice-free? The answer to these questions form the foundation to evaluate whether the recent and ongoing polar ice sheet response to global warming might be the dawn of ice sheet collapse and potential abrupt sea level rise, which would represent a disaster of epic dimension for our society at a time when most of earth's population lives near coastal margins. From that perspective, cosmogenic nuclide techniques applied to glacial landscapes can contribute fundamental information toward sustainable development of our ever-growing society on a rapidly warming planet.

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Ice Cores

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Introduction

Ice cores from Antarctica, from Greenland, and from a number of smaller glaciers around the world yield a wealth of information on past climates and environments. Ice cores offer unique records on past temperatures, atmospheric composition (including greenhouse gases), volcanism, solar activity, dustiness, and biomass burning, among others. In Antarctica, ice cores extend back more than 800,000 years before present (Jouzel et al. 2007), whereas Greenland ice cores cover the last 130,000 years (Dahl-Jensen et al. 2013). A few ice cores from high-elevation glaciers in the Himalayas (Thompson et al. 1997) and in the Andes (Thompson et al. 1998) extend back into the last glacial period, whereas most other ice cores from lower latitudes are constrained to the Holocene period (last 11,700 years). In order to make proper interpretation of ice core records, it is essential to establish accurate and precise ice core chronologies that assign an age to each depth segment of the core.

Under favorable conditions, the annual signal in ice cores can be traced thousands of years back in time. The temporal resolution of ice cores is generally high compared to that of other paleoarchives, such as marine and lacustrine sediments, stalagmites, and tree rings (Ruddiman 2008). The annual accumulation on glaciers ranges from a few centimeters of ice per year in high-elevation areas of Antarctica to several meters of ice at coastal sites and at lower latitudes. In the upper part of an ice sheet, snow compacts to incompressible ice in a transition zone known as the firn. Due to the continuous accumulation of snow, annual layers become buried in the ice sheet with time, and due to a general flow of ice toward ice margins, annual layers are thinned with depth (Fig. 1). Close to the base of an ice sheet and close to ice margins, the stratigraphy is often disturbed as the ice is pushed over bedrock undulations.

Ice Core Dating Methods

Ice core chronologies are based on a number of different techniques that include annual layer counting, use of well-dated reference horizons, glaciological modeling, and “orbital tuning” where ice core records are linked to well-known temporal variations of the Earth’s orbit. Often several techniques are combined to produce the optimal ice core chronology (Cuffey and Paterson 2010). In regions with significant surface melt, such as low-latitude glaciers or coastal regions, ice core dating may be particularly challenging as the stratigraphy will be disturbed to some degree.

Layer Counting

An annual signal in ice cores may be preserved in the isotopic composition of the ice itself or in ice impurities such as terrestrial dust or ionic species. The isotopic ratios $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ of the most

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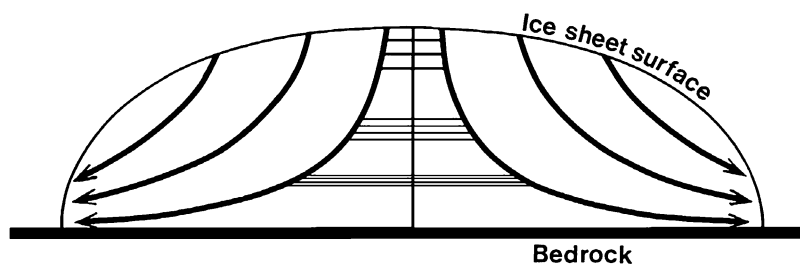


Fig. 1 Schematic cross section of a large glacier such as the Greenland ice sheet. *Thick arrows* indicate the main ice flow pattern, and *horizontal lines* represent descending annual layers that are stretched and thinned over time due to ice flow. The most well-preserved ice core profiles are obtained from the central part of the ice sheet where the ice flow is mostly vertical, and there is no melting

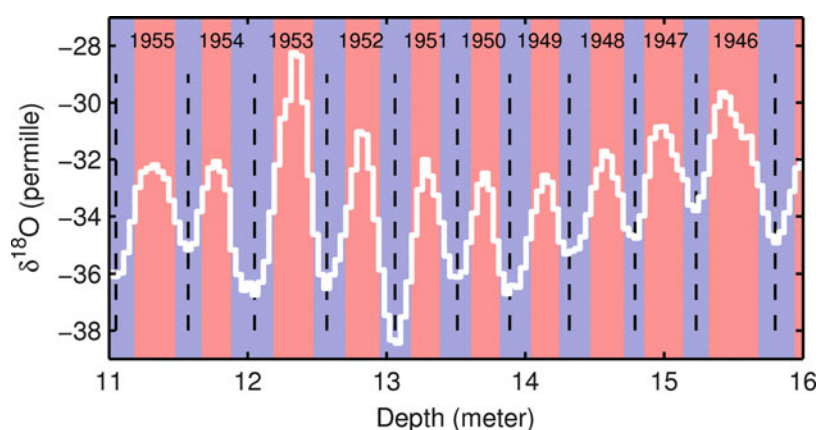


Fig. 2 A five meter section from a Central Greenland ice core showing annual layers in the stable water isotopes ($\delta^{18}\text{O}$). High $\delta^{18}\text{O}$ values are summer layers, and low values occur during winter. The ice core is dated by annual layer counting from the surface, and the shown depth interval covers the time period 1946–1955 AD. At high-accumulation sites, annual layers can be identified in ice cores water isotopes thousands of years back in time (Figure from www.iceandclimate.nbi.ku.dk)

abundant stable water isotopes in glacier ice are related primarily to the local temperature at the time of precipitation (Dansgaard et al. 1969). They therefore vary over the seasons and preserve a signal of the annual cycle (Fig. 2). The isotopic ratios are normalized with respect to a standard and reported as $\delta^{18}\text{O}$ for oxygen and $\delta^2\text{H}$ (or δD) for hydrogen. At high-accumulation sites, the annual signal of those isotopes may be traced several thousands of years back in time (Vinther et al. 2006). At lower accumulation sites, however, diffusion of water molecules in the firn reduces or completely erases the seasonal variation (Johnsen et al. 2000). Furthermore, layer thinning caused by ice flow eventually makes the water isotopic seasonal cycle disappear with depth.

Ice core impurities, such as terrestrial dust and sea salt, often express a seasonal cycle in ice cores. For example, at present, Greenland dust generally shows a maximum during springtime, whereas sea salt peaks during winter (Kuramoto et al. 2011). The dust annual cycle may even be observed directly in the visual stratigraphy of the ice core (Alley et al. 1997; Fig. 3). Because dust particles are fixed in the ice matrix, they are less vulnerable to diffusion than water isotopes and ionic species, and they, therefore, preserve annual layers much further back in time. Extensive high-resolution dust and

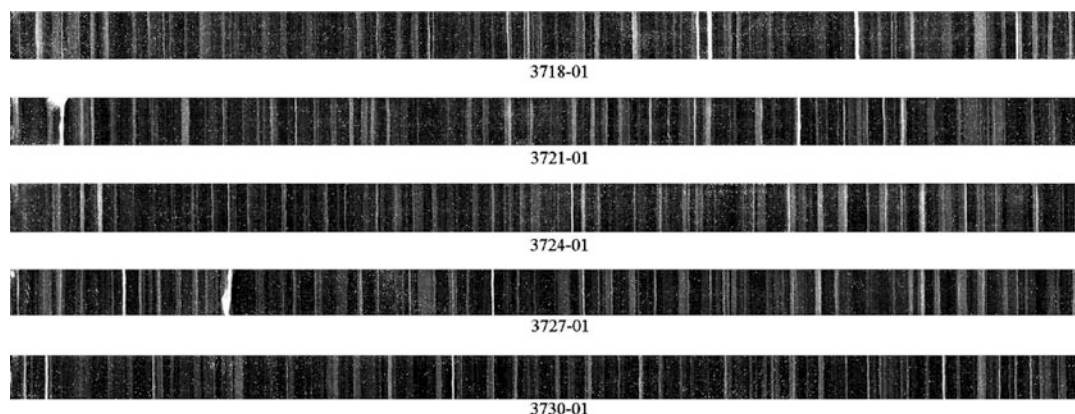


Fig. 3 The annual layering of the Greenland ice sheet is visible to the naked eye. This example shows 5×1.65 m sections of visual stratigraphy from 2050 m depth in the NGRIP ice core from Central Greenland. At this depth, the ice is some 38 thousand years (ka) old, and the shown sections cover some 275 years of precipitation. The image is obtained with indirect illumination of the ice core so that black areas correspond to clear ice, whereas white layers contain elevated amounts of dust (Data from Svensson et al. 2005)

chemical impurity datasets from several deep Greenland ice cores have allowed for multi-proxy layer counting and tracing of annual layers well into the last glacial period (Andersen et al. 2006).

The strength of the layer-counted time scales lies in the very well-constrained event durations that allow precise determination of the sequence of events and of the exact event duration of past climate change (Steffensen et al. 2008). On the other hand, the counting error of counted time scales increases with age making the absolute error fairly large compared to other dating methods. Recently, automated methods for annual layer counting in ice cores have become available (Winstrup et al. 2012), which may play a more important role in future ice core chronologies. Annual layer counting has been applied to ice cores worldwide, but Central Greenland and coastal (high-accumulation) sites in Antarctica are the only sites where annual layer counting is feasible in the early Holocene and in the last glacial period.

Stratigraphic Linking

Numerous well-dated volcanic eruptions have left traces in ice cores, sometimes in the form of ash particles or “tephra” (Abbott and Davies 2012; Narcisi et al. 2012) but more often in the form of elevated acidity levels (mostly sulfuric acid) (Fig. 4). For example, the well-known 1815 AD Tambora eruption (Indonesia) has been identified as an acidity spike in many ice cores. During the last glacial period, the North Atlantic Ash Zones I and II provide important tephra marker horizons for Greenland at 12 and 38 ka before present, respectively, whereas Mt. Berlin is a central reference tephra layer in Antarctica at 92 thousand years before present (ka BP). Besides providing information on the timing and magnitude of past eruptions, ice core acidity spikes are also widely used for synchronization of ice cores. All of the deep Greenland ice cores are thus synchronized throughout the last glacial cycle based on numerous volcanic markers (Rasmussen et al. 2008; Vinther et al. 2006), and within Antarctica ice cores are being linked in a similar way (Parrenin et al. 2012; Severi et al. 2007).

A number of different approaches have been taken to synchronize ice cores from Greenland with those of Antarctica whereby climate change can be studied on a global scale. The air bubbles in ice

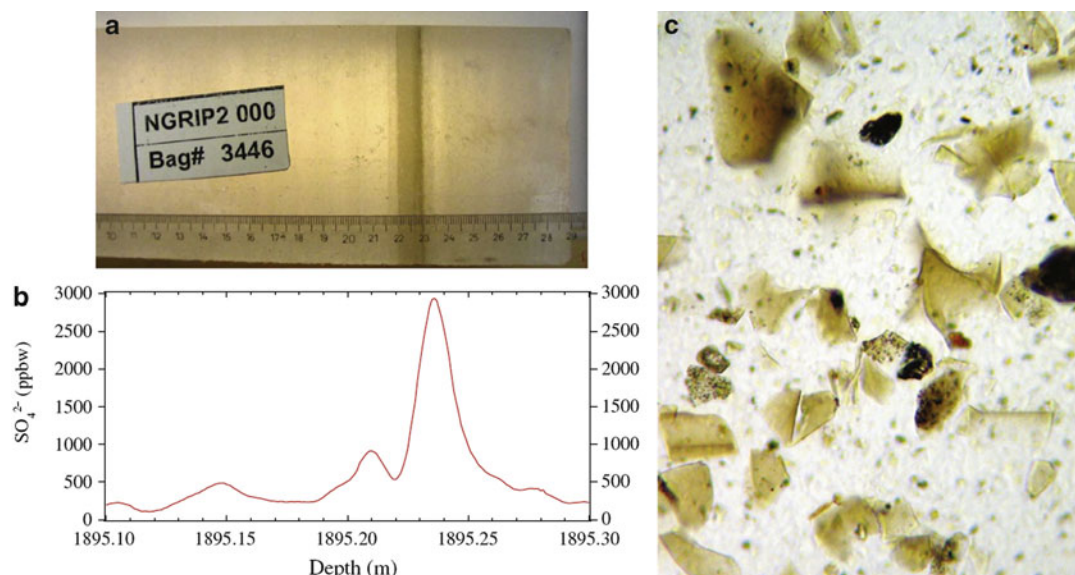


Fig. 4 Example of a visible tephra layer from the Icelandic Katla volcanic in the Greenland NGRIP ice core. The layer is from 1895.24 m depth and has an age of about 29 ka. **(a)** The visible tephra horizon in the ice core. **(b)** The associated sulfate peak in the ice. **(c)** Basaltic glass shards from the eruption as found in the ice core (Figure modified from Abbott and Davies 2012)

cores from both hemispheres share a global signal of well-mixed atmospheric gases. For example, methane concentrations show great variability over the last glacial period and can be applied for bipolar ice core matching (Blunier and Brook 2001; EPICA Community Members 2006). Also the global signal of oxygen isotopes of air trapped in ice cores can be applied to match ice cores from the two hemispheres (Bender et al. 1994; Capron et al. 2010). Bipolar volcanic matching of ice cores is feasible when large low-latitude eruptions inject great quantities of acid into the stratosphere. Over the last two millennia, where ice cores are precisely dated, some 50 bipolar volcanic events have thus been identified (Sigl et al. 2013). Greenland and Antarctic ice cores are also synchronized at the time of the largest volcanic eruption of the last million years, the Toba eruption (Indonesia) occurring some 74 ka before present (Svensson et al. 2013). Furthermore, the global signal of cosmogenic ^{10}Be in ice cores has been applied to match Greenland and Antarctic ice cores at the Laschamp geomagnetic excursion that occurred about 41 ka ago (Raisbeck et al. 2007).

Orbital Tuning

On time scales of tens of thousands of years, the Earth's climate is modulated by orbital variations that influence the solar insolation distribution on Earth. Several parameters measured in ice cores are shown to vary with the orbital parameters that are known with high accuracy (Laskar et al. 2004). The older section of Antarctic ice cores is dated by tuning the ice core record variability to that of the orbital parameters applying so-called orbital tuning (Fig. 5). The ice core records expressing variability on orbital time scales include the oxygen isotope ratio of air bubbles (Landais et al. 2010; Sowers et al. 1989), the O_2/N_2 ratio of air bubbles (Bender et al. 1994; Kawamura et al. 2007), and the total air content of the ice (Raynaud et al. 2007). Unfortunately, the linking between orbital forcing and the ice core records is rather poorly

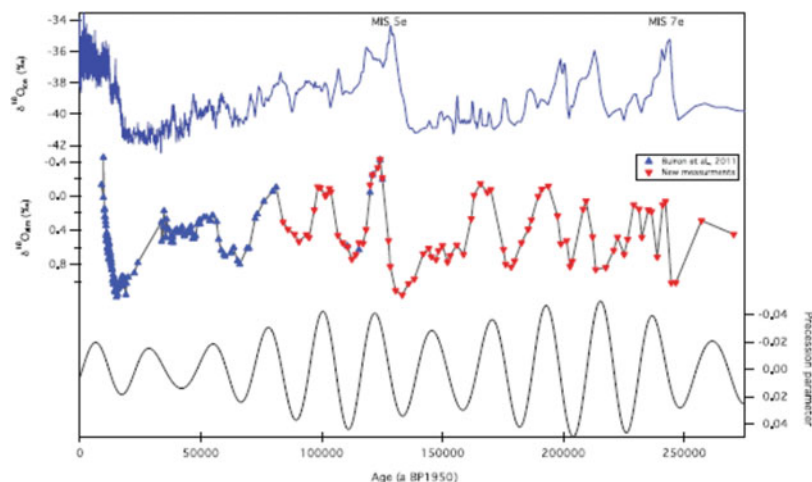


Fig. 5 Example of orbital tuning of the Antarctic TALDICE ice core for the past 250 ka. *Top*: stable water isotopes of the ice ($\delta^{18}\text{O}_{\text{ice}}$) with labeling of interglacial periods (MIS5e and MIS7e). *Middle*: stable water isotopes of the gas record ($\delta^{18}\text{O}_{\text{atm}}$) with colors referring to different datasets. *Bottom*: the Earth's orbital precession parameter that partly controls the $\delta^{18}\text{O}_{\text{atm}}$ and that is used for tuning the time scale (Figure from Bazin et al. 2013)

constrained. Therefore, the use of orbital tuning for ice core dating implies uncertainties of thousands of years (Bazin et al. 2013).

Glaciological Modeling

In the deeper part of the large ice sheets and at locations where annual layers are not available, ice core age scales are based on modeling. To model an ice core time scale, it is needed to reconstruct (1) past accumulation rates and (2) the thinning of annual layers with depth. In polar regions, accumulation rates are to first order linked to temperatures that may be estimated from temperature proxies, such as stable water isotopes ($\delta^{18}\text{O}$ and δD). However, many other parameters influence the accumulation as well, for example, past ice sheet elevation changes, “upstream effects” (i.e., due to ice flow, the ice in the deeper part of an ice core must be traced back to its origin at the surface), and changes in the precipitation source(s). The ice flow may be simulated by simple one- or two-dimensional approaches (Johnsen and Dansgaard 1992) or by sophisticated 3D models that take into account many of the physical properties of the ice sheet, such as ice temperatures, ice impurity content, ice crystal texture, and basal melting (Ritz et al. 2001). Generally, many of those properties are poorly known, and modeled ice core chronologies are often constrained by other dating methods, such as age markers or orbital tuning. The most recent ice core age models use inverse methods and combine records from several ice cores and their stratigraphic links to produce a consistent chronology common for all the cores (Bazin et al. 2013).

Radiometric and Other Dating Methods

Currently, radiometric methods have rather limited applications for ice core dating. Atmospheric testing of nuclear weapons has produced reference horizons in 1950–1960 that can be detected as elevated beta-activity of ice. Young ice can be dated by ^{210}Pb or ^{32}Si counting, but the precision

cannot compete with that of annual layer counting. Due to a significant in situ production, ice cores can generally not be dated by ^{14}C (Petrenko et al. 2013) unless the ice contains sufficient biogenic material (Jenk et al. 2009). As a consequence, ice core time scales and ^{14}C calibration curves may not be entirely compatible during the last glacial period (Muscheler et al. 2008). The cosmogenic isotopes of ^{10}Be and ^{36}Cl can be measured in ice, but due to long half-life times and poorly constrained production rates, they mostly have applications for age estimation of very old ice, such as basal ice. The Matuyama-Brunhes (M-B) geomagnetic reversal observed as a ^{10}Be minimum at 776 ka is applied as a reference marker to constrain ages of the oldest Antarctic ice cores (Raisbeck et al. 2006).

Recently, developments have been made toward dating Antarctic ice cores based on the accumulation of ^{234}U in the ice matrix from recoil during ^{238}U decay out of dust bound within the ice (Aciego et al. 2011). Also ^{81}Kr may have a potential for dating of old ice, but its abundance in glacier ice is very low (Jiang et al. 2012). The age of basal ice containing material from bedrock (silty ice) can be estimated by a number of alternative methods such as $^{10}\text{Be}/^{36}\text{Cl}$ isotope ratios, optically stimulated luminescence, amino acid racemization, and maximum likelihood estimates for the branch length of the invertebrate cytochrome oxidase subunit I sequences (Willerslev et al. 2007).

Gas Record Chronologies

An important issue for ice core time scales is that of dating the air bubbles enclosed in ice cores. The snow or firn in the upper part of an ice sheet is generally permeable to air, and air bubbles are only permanently enclosed in the ice at the so-called lock-in depth that occurs typically at 50–100 m depth when snow compacts to ice. Because of the mixing of air in the upper part of the ice sheet, the age of air in an ice core sample is always younger than that of the encapsulating ice (Schwander et al. 1993). This difference in age between the air bubbles and surrounding ice is site specific and depends mainly on past accumulation rates and temperatures (Goujon et al. 2003). The gas-ice age difference varies from a few decades at present-day high-accumulation sites to several millennia at low-accumulation sites during glacial periods (Loulergue et al. 2007). The age difference can be constrained by modeling and by isotopic measurements of air molecules that respond to temperature gradients in the snow during bubble formation (Severinghaus and Brook 1999). Because it is important to link the climate signal of the ice to that of the atmospheric composition contained in the air bubbles, there are generally two age scales associated with an ice core: one for the ice and one for the gas records.

Greenland and Antarctic Ice Core Chronologies

Numerous chronologies have been made available for Greenland ice cores over the last decades (Southon 2004). Today, all of the deep Greenland ice cores (DYE-3, GRIP, GISP2, NGRIP, NEEM, Camp Century, Renland; see references in Johnsen et al. (2001)) are on a common time scale named the Greenland Ice Core Chronology 2005 (GICC05). This time scale is based on layer counting in several ice cores and covers the last 60,000 years (Svensson et al. 2008). For the most recent 8000 years, GICC05 is based on counting of annual layers in the water isotopic signal (Vinther et al. 2006), whereas dating of the older part is based on layer counting in dust and other impurities in the ice (Andersen et al. 2006; Rasmussen et al. 2006). The GICC05 time scale is associated with a counting uncertainty that provides an error estimate. The absolute error is around 1 % in the Holocene and about

5 % in the last glacial period. GICC05 has been extended with an ice flow model to cover the 123,000 time span of the Greenland ice cores (Wolff et al. 2010). The Greenland ice cores are internally synchronized using common volcanic reference horizons (Rasmussen et al. 2008), and tephra is used to link the Greenland ice cores to other paleoarchives (Abbott and Davies 2012; Blockley et al. 2012).

For Antarctica, individual time scales have traditionally been developed for each of the deep ice cores (Byrd, Vostok, EDC, Dome Fuji, EDML, TALDICE, Law Dome, Taylor Dome, see references in Stenni et al. (2010)). The time scales are mostly based on ice flow models that are constrained by stratigraphic markers and orbital tuning (Kawamura et al. 2007; Parrenin et al. 2007). Recently, inverse methods have been applied to integrate several Antarctic ice core chronologies with those of Greenland (Lemieux-Dudon et al. 2010). The most recent ice core time scale for Antarctica is the Antarctic Ice Core Chronology 2012 (AICC2012) that applies to several deep Antarctic ice cores (Bazin et al. 2013; Veres et al. 2013). For the last 60,000 years, AICC2012 is synchronized to the Greenland ice cores through their global gas concentration records and through bipolar volcanic and geomagnetic events. For the older part, AICC2012 is constrained by independently dated tephra layers, by orbital tuning, and by the B-M geomagnetic boundary. For the last glacial cycle, the AICC2012 error estimate is similar to that of Greenland time scales, and beyond that the accuracy is within 5000 years back to the M-B boundary. It is expected that more Antarctic ice cores will be integrated with the AICC2012 time scale and that a new layer-counted time scale will become available from the recently recovered WAIS ice core reaching back to 68 ka (WAIS Divide Project Members 2013).

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Lacustrine Environments (^{14}C)

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Synonyms

Radiocarbon

Definition

Lacustrine. Having to do with any part of a lake system.

Introduction

Lakes are extremely powerful archives of climate and environmental information, because they record changes in the landscape around them, and the records they preserve are thus directly relevant to the activities and environments of human societies (e.g., Adams et al. 2008). Lakes commonly have very high sedimentation rates (5–20 years/cm) and preserve biological, geochemical, and sedimentary proxies and therefore may contain highly detailed records of past change. However, lakes are also dynamic sedimentary systems, and steady, continuous sedimentation may be disrupted by floods, lake-level changes, slope failures, and seismic shaking (e.g., Smith et al. 2013). Along with sedimentary fabric, radiometric dating is the best way to identify missing or repeated sections (Grimm 2011) and to identify and quantify changes in sedimentation rate.

Radiocarbon dating is the technique most often used to build age models for proxy records of paleoenvironmental change over the last ~40,000 years. Identifiable terrestrial organic plant macrofossils are the gold-standard material for dating, because they are most closely tied to the coeval atmospheric ^{14}C content and least susceptible to postdepositional chemical alteration (Staff et al. 2011). The frequent paucity of terrestrial macrofossils, however, means that often other materials must be used. These materials should be carefully evaluated in comparison to independent age information.

The high throughput and small sample size of modern accelerator mass spectrometer (AMS) measurements of ^{14}C has been a boon to the development of lacustrine age models, permitting them to potentially match the centennial to decadal resolution of many proxy records. Unfortunately, radiocarbon analyses remain expensive relative to most proxy measurements, and the analytical precision is often degraded by calibration from ^{14}C years to calendar years, which is required to account for changes in atmospheric ^{14}C content through time. Tremendous sustained community effort has produced a robust, precise international calibration curve covering the entire range of ^{14}C dating from 0 to 50 ka (IntCal13, Reimer et al. 2013). The advent of user-friendly computer programs for application of Bayesian statistics to ^{14}C -based age-depth models (Blaauw and Christen

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2011; Bronk Ramsey 1995; Bronk Ramsey and Lee 2013) in combination with the calibration curves enables the production of robust and relatively high-precision radiocarbon-based age models.

Sources of Carbon to Lakes

Carbon in lakes may be brought as dissolved or particulate carbon in surface water, groundwater, or springs, as organic molecules or particles recycled within the lake water, biota, and sediments, and through gas exchange with the atmosphere at the lake surface (Abbott and Stafford 1996; Jull et al. 2013; Alberic et al. 2013). In areas with ancient carbonate bedrock or old carbonate-rich surface material (e.g., lake sediments or glacial till), the dissolved carbon in surface waters is frequently depleted in or devoid of ^{14}C , and the flux of carbon to the lake water from other sources may overwhelm the rate of gas exchange with the atmosphere, producing the hard-water, or reservoir, effect (Deevey et al. 1954; Broecker and Walton 1959).

In addition, even where the bedrock does not contain carbonate minerals, groundwater that has been isolated from the atmosphere may have undergone significant radioactive decay of ^{14}C , the lacustrine equivalent of ^{14}C -depleted “old” deep water in the ocean. The oxidation of organic material deposited in a lake may also introduce old carbon to the lake water, as dissolved organic carbon (DOC). Finally, deeply circulating hot springs may introduce ^{14}C -dead geothermal fluids into a lake system (Oremland et al. 1987). Although this source is easy to rule out in many places, in tectonically active regions it may be a highly variable effect, as the flow rate from springs may change suddenly and drastically in response to tectonic forces. In lakes affected by any of these processes, the dissolved inorganic carbon (DIC) pool in the lake water, from which aquatic plants and animals and inorganic carbonates get their carbon, may be hundreds or thousands of years out of equilibrium with the coexisting atmosphere and variable through time (Deevey et al. 1954).

Sample Selection

The desire for radiocarbon-based age models to give the calendar year of events recorded in lake sediments sets several requirements for choosing appropriate materials for dating:

1. The ^{14}C content of the material should be that of the atmosphere in the year of its formation.
2. The material should be deposited in the lake sediment as soon as possible after isolation from the atmosphere (i.e., death of plant/animal).
3. The C-isotope composition of the material should not have changed after its deposition.

Thus, the best material is identifiable terrestrial plant material: needles, leaves, twigs, seeds, etc., and charcoal from these materials, along with insect parts that are identifiably terrestrial. In general, the best assurance of the nearly immediate deposition of the material is to select delicate macrofossils, such as leaves, which are unlikely to survive storage or reworking. However, it is quite common for lake sediments to be lacking in sufficient terrestrial material, especially in landscapes with sparse vegetation such as the Arctic (Saulnier-Talbot et al. 2009) and dry lands, Plazcek et al. (2006) as well as in cores from the depocenter of large lakes (Shanahan et al. 2013). The lack of sufficient high-quality datable material is a problem that increases with the need for large numbers of dates to build high-resolution age models. As a result, many investigators are left choosing between less desirable alternatives, each with its own drawbacks.

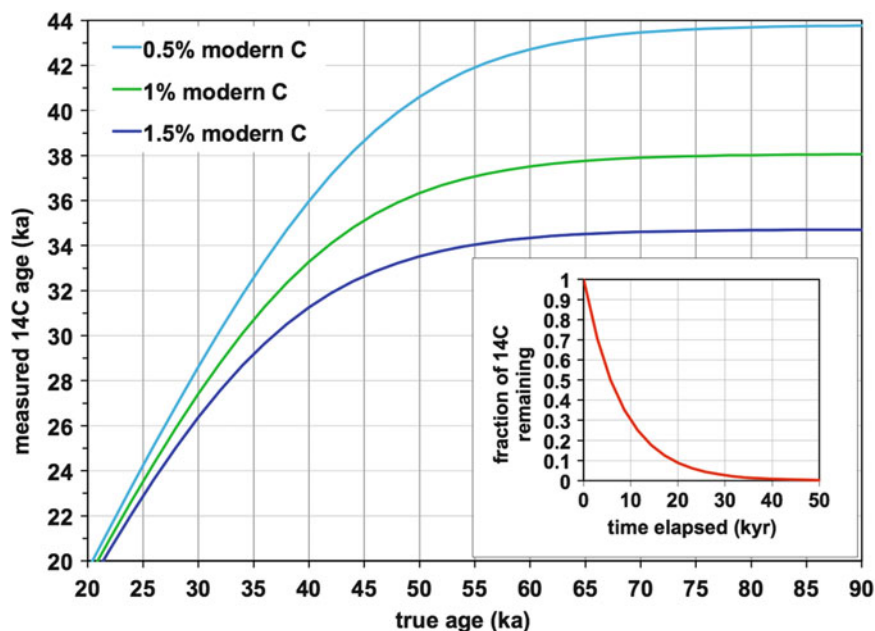


Fig. 1 Effect of small amounts of modern ^{14}C on increasingly old materials; with only 1 % modern carbon, all infinite-age materials will appear to be ~ 38 ka. (*Inset*) By 40 ka < 1 % of the original ^{14}C remains

Dating of pollen concentrated from sediments has been proposed by several authors, using a number of different methods to separate the pollen from other organic or inorganic sources of carbon (Brown et al. 1992; Mensing and Southon 1999). A recent development is the application of flow cytometry, developed to sort cells for biological applications, to the sorting of pollen (or microcharcoal) from a sediment sample (Tennant et al. 2013). Flow cytometry can separate millions of grains in a few hours, making the sorting of samples large enough for ^{14}C analysis straightforward, especially in settings with abundant sources of large pollen (e.g., *Pinus*). However, comparisons between pollen and other kinds of dates show mixed results (Newnham et al. 2007; Neulieb et al. 2013). With the easier application of pollen dating potentially enabled by flow cytometry, it may be that the main sources of difficulty (non-pollen matter, reworked pollen, etc.) can be identified and overcome in suitable cases.

Aquatic plant parts (Marty and Myrbo *in press*) and shells are secondary alternatives to terrestrial material, as they are produced from dissolved inorganic carbon (DIC) in the lake water, which may be older than the coeval atmosphere for reasons listed in the previous section. Plant material is preferred to shells because contaminating carbonate and organic acids are removed by chemical pretreatment (see “► 14C dating” entry), and it is as resistant to postdepositional alteration as terrestrial plant material. Carbonates require an additional caution, as calcium carbonate minerals (e.g., aragonite, calcite) are quite soluble and thus are easily altered after deposition. Mineralogical and microscopic examination of shells is important, especially in shells expected to be more than 20,000 years old, where even small amounts of younger carbon can have a large effect on the apparent age (Fig. 1).

In addition to the reservoir effect (making ages too old) and the possibility of alteration, carbonates exposed by lake-level drop may adsorb young carbon from the atmosphere or shallow groundwater. This “modern carbon” effect (Fig. 2) has the opposite influence as the reservoir effect, making dates too young; thus the true magnitude of each effect may be masked by the other (Zimmerman et al. 2012; Plazcek et al. 2006).

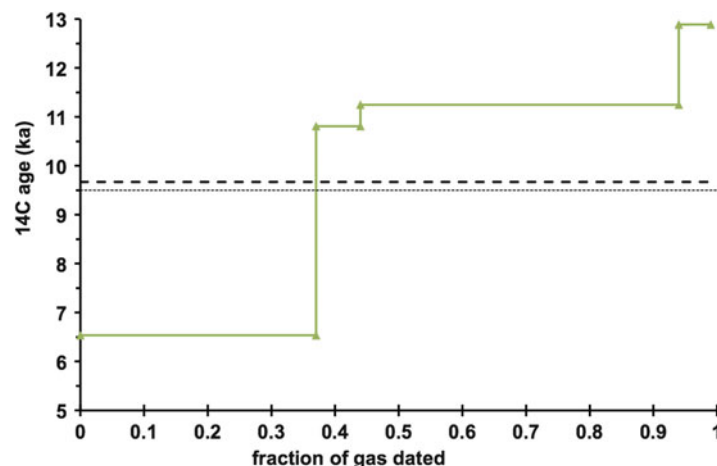


Fig. 2 Progressive dissolution experiment on late Pleistocene ostracodes (Zimmerman et al. 2012). ¹⁴C dating of CO₂ fractions evolved during reaction of ostracodes with acid shows large component of young ¹⁴C on outer surfaces. The true age of the ostracodes is the age of the last step *or older*; dotted line shows the integrated ¹⁴C age of ostracodes from the same sample (measured separately)

With these considerations in mind, carefully selected and prepared aquatic plants and shells (Pigati et al. 2010; Myrbo et al. 2011; Marty and Myrbo *in press*) can yield robust ¹⁴C analyses. However, it is still critical to remember that aquatic materials may hide a variable lake reservoir effect, when interpreting their ¹⁴C ages as dates. Pairing the dates on aquatic material to a few terrestrial ¹⁴C dates or other known ages at the same level in the sediment sequence may provide some measure of confidence and a basis for estimating a reservoir correction.

In lakes with little else to date, bulk sediment measurements should be used only with extremely close attention to the multiple processes affecting the cycling of carbon in the particular lake and only when measurements at several depths in the sediment column show a relatively consistent offset with independent age markers such as terrestrial macrofossils or well-dated tephra (Blaauw et al. 2011). All of the sources of solid and dissolved carbon discussed in the previous section may influence the carbon isotope chemistry of the sediment, and additional sources of old carbon may be region or lake specific and difficult to identify (e.g., Grimm et al. 2009; Colman et al. 1996). Most importantly, the kind and amount of organic matter, the degree and frequency of oxygenation, and rise and fall of lake level (natural or anthropogenic) all affect the carbon isotope composition of the bulk sediment, and all are likely to be changing through time.

A Word About Outliers

Radiocarbon ages that “look wrong” in the context of the whole dataset should be carefully examined, and there should be some basis for rejection of outliers that are <3-sigma different from the expected age. A few common causes of suspicious dates may include the following. Samples taken from too close to the core edge, top, or bottom, from a zone of disturbance, or from the core catcher may be too young or too old and can be rejected (and avoided in the future). Unidentified plant parts that are too old may be aquatic and indicate that the water had a reservoir age at the time the plant grew (regardless of the modern situation). Charcoal or wood that is too old may have been stored on the landscape before deposition or be from the interior of a long-lived tree.

Aside from coring disturbance, it is relatively difficult to make a radiocarbon sample too young. Small (<0.3 mg) or old samples (>20,000 years, depending on sample size and precision required) contain small amounts of original ^{14}C and therefore are more sensitive to contamination by small amounts of modern carbon. This may be from contamination by carbonate or microbiological growth (Wohlfarth et al. 1998) or simply from exposure to the atmosphere. Concurrent preparation of matrix-matched, similarly sized background materials is a critical tool for monitoring these effects.

Building an Age Model

A key consideration when building an age model for lacustrine sequences is the time resolution it provides for interpretation of the proxy records. The high sedimentation rates in many lakes provide an unparalleled view of paleoenvironmental change, but the number of dates in the accompanying age model is often an order of magnitude or even two lower than the proxy measurements. This mismatch results in a situation where decadal or centennial interpretations and correlations of proxies are made, when only millennial-scale time resolution is available.

Radiocarbon ages are reported, like most isotopic measurements, as values with some analytical uncertainty that is normally distributed about the measurement value; typical ^{14}C measurements made by AMS are reported with a 1-sigma analytical uncertainty of 20–40 years. The additional step of calibration to calendar years introduces a nonuniform probability to ^{14}C -based calendar ages, however, because of plateaus and reversals in the slope of the calibration curve (Reimer et al. 2013). That is, within the calibrated range of a ^{14}C measurement, some calendar years will be much more likely than others, and many ^{14}C ages have multiple ranges, separated by calendar years with zero probability (Fig. 3).

The information in the probability density function is not captured by simple linear or spline fits to a series of age-depth points nor by the practice of reporting a central or highest-probability age and the oldest and youngest ends of the ranges. In the usual lacustrine age model of 5 or 10 dates or more, it becomes impossible to express the precision with which the timing of a shift or event in the proxy records is known, unless it coincides in depth with a radiocarbon age measurement.

Programs such as OxCal (Bronk Ramsey 1995) and Bacon (Blaauw and Christen 2011) use Bayesian methods to take advantage of prior information (priors) about a sediment sequence, including stratigraphic order, the relative timing of events, and the location of hiatuses in the sequence, as well as the fact that the probability of any calendar year within the calibrated range varies (Bronk Ramsey 2009). Many thousands or millions of iterations of Monte Carlo analysis are used to define the probability of any depth in the sediment being equivalent to a particular calendar year (Fig. 4). This is especially powerful for defining the precision of an age model between dated horizons and for choosing locations in the sediment sequence where additional dates will provide the most valuable information.

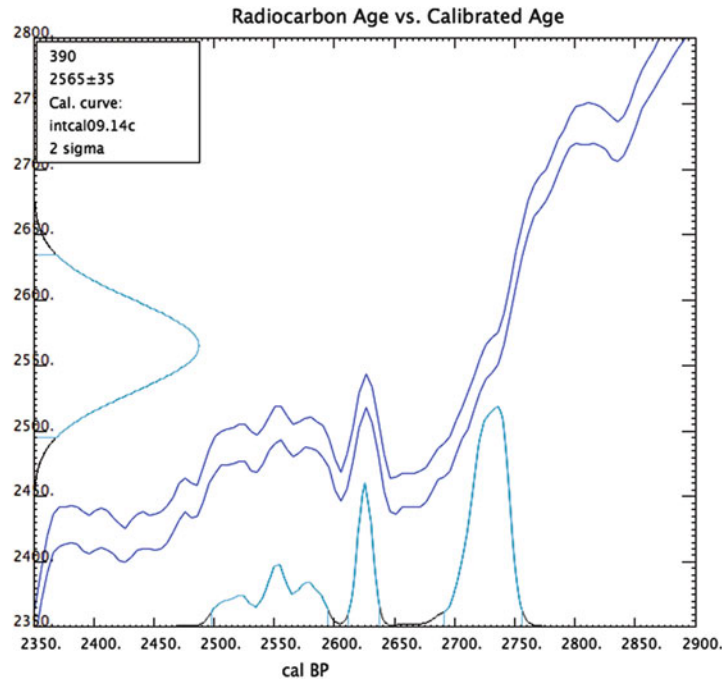


Fig. 3 Probability density function produced by calibration of a ^{14}C age of 2565 ± 35 years before present (*left axis*); wiggles in the calibration curve (*diagonal line*) produce windows of ages with high and low probability (*bottom axis*), rather than an equal likelihood of any age within the calibrated range. Figure made with Calib 6.0 (Stuiver et al. 2005 ref)

Summary

Advances in AMS sample preparation and measurement and Bayesian modeling software enable construction of robust, relatively high-precision and high-accuracy radiocarbon age models to support the high-resolution, multi-proxy lake records that have proliferated recently. Fundamentally, radiocarbon chronologies require an investment in a sufficient number of ages to support the time resolution of the proxy-record interpretations. Furthermore, they must include acknowledgment of the geological uncertainties inherent to all sample types. While identifiable terrestrial macrofossils remain the preferred material for radiocarbon dating, reliable age models can be based on other materials, where careful consideration of pre- and post-depositional effects on the carbon is combined with application of as many chronological techniques as possible.

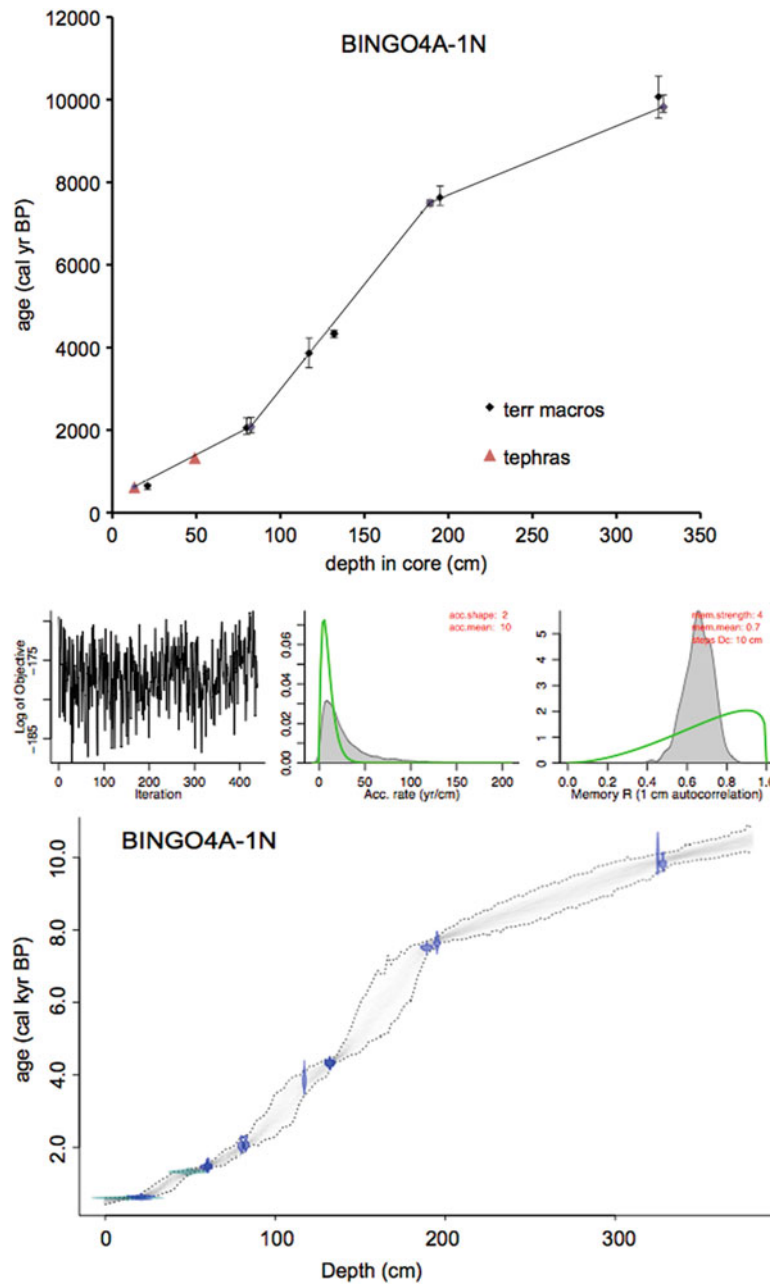


Fig. 4 Age model for a lake core built using the Bayesian-based program Bacon (Blaauw and Christen 2011). Purple shapes represent probability density functions for ¹⁴C dates; green ellipses are independently dated tephras. Dotted lines enclose envelope of 95 % confidence interval, with darker gray shading for depths with higher confidence intervals. Additional dates between 120 and 300 cm depth would greatly improve the precision of the age model

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Marine Varves

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Synonyms

[Annually laminated sediments](#); [Laminated sediments](#); [Rhythmites](#)

Definition

The term varve is a Swedish word that means cyclic layer. It was first used in 1862 as *Hvarfig lera* by the Swedish Geological Survey to describe rhythmically deposited light and dark clay layers in a proglacial environment on one of the first geological maps of Sweden.

Introduction and History

The study of varved sediments extends back more than 150 years, when alternating pale and dark laminations in marine and lacustrine sediments in Europe and North America were first mapped and interpreted as a potential source of chronological information. The concept of annually laminated sediments was later developed by Swedish geologist De Geer, who applied the chronological information stored in varved clays deposited near the margin of the retreating Scandinavian ice sheet to determine the time elapsed since the termination of the last glacial period. De Geer established a network of sites along the Baltic coast of Sweden and linked them using recognizable variations in varve thickness (De Geer [1912](#)). In addition, he defined the term varve as being one complete annual cycle consisting of a coarse-grained pale summer layer and a fine-grained dark winter layer. Finally, De Geer coined the term geochronology and for the first time introduced a temporal unit (the year) to geology (De Geer [1912](#)). Following his work, varve research expanded to include a broad range of types with applications to different scientific disciplines.

Varve Formation and Preservation

Varved sediments are created primarily through the interplay of two processes: seasonal variations in the genesis, transport, and deposition of sediments and the preservation of that signal after burial. A strong seasonal cycle that influences sedimentation is the fundamental process controlling varve deposition. In most settings this is not a limiting factor because a dominant seasonal climate cycle with large impacts on the environment, particularly the hydrological cycle, can be found nearly everywhere. In temperate climates, for example, surface water runs freely in summer and freezes over in winter, greatly varying the amount of energy available for clastic sediment transport. Similarly, in the tropics, monsoons create dramatically different runoff during wet and dry seasons.

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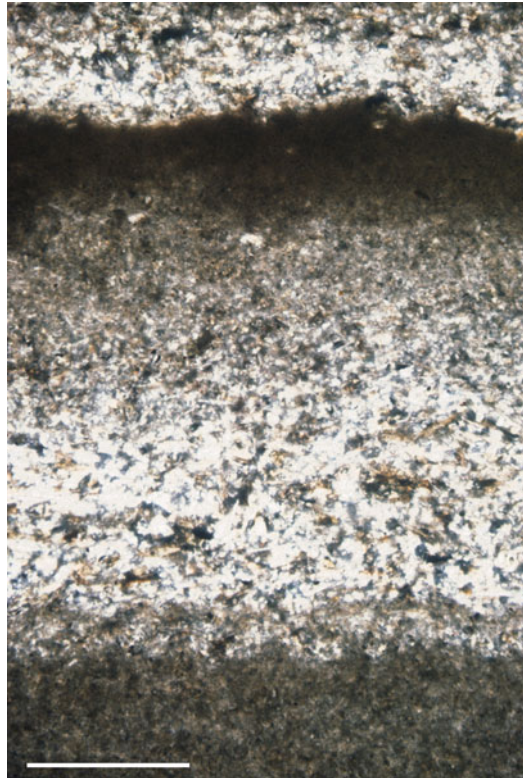


Fig. 1 Photomicrograph of clastic varve couplets from glacial Donard Lake, Baffin Island, core 95DON-05, 47 cm. The sediment surface is toward the *top* of the photo. Scale bar is 1 mm (Photograph: K. Hughen)

Of course, biology also follows seasonal cycles, and this influences sedimentation. Diatoms in freshwater lakes bloom during spring and summer and die out in winter, and production based on marine upwelling may fluctuate seasonally following movements of zonal winds. Such manifestations of seasonality result in different sedimentary regimes, delivering biological or mineralogical material to the sediment surface at different times of year as distinct layers.

Seasonal sediment layers are produced and deposited in many environments but are usually disturbed by bioturbation from benthic organisms, as well as sediment mixing and resuspension due to slumping and current action. In order for varves to be preserved, the fragile seasonal layers must remain intact after deposition. In lakes, morphometry of the basin is one of the most important features controlling laminae preservation and the potential for sediment disturbance. A relationship exists between lake area and depth in those sites with preservation of laminated sediments (O'Sullivan 1983). In general, very deep lakes or lakes that have great *relative* depth will avoid deep wind mixing and allow development of strong thermal stratification. Deep lakes, thus, experience reduced resuspension of surface sediments and, importantly, ventilation of bottom water. Oxidation of organic matter falling through the water column then depletes available oxygen and the deep waters become anoxic, preventing the growth of benthic organisms and the influence of bioturbation. Physical isolation of bottom waters can also occur in the ocean, in shallow-silled marine basins formed as deep fjords such as the Saanich Inlet, British Columbia (Blais-Stevens et al. 1997), or as tectonic basins such as the Santa Barbara Basin, California (Behl and Kennett 1996); Cariaco Basin, Venezuela (Peterson et al. 2000); and Guaymas Basin, Gulf of California (Calvert 1966). Water column stratification occurs due to chemical as well as thermal processes, such as can be found in coastal tidewater lakes where saltwater introduced at high tides is overlain

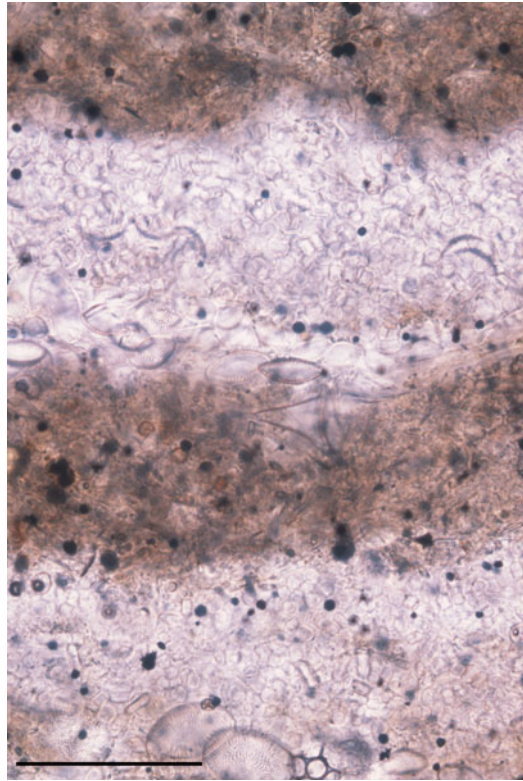


Fig. 2 Photomicrograph of biogenic varve couplets from Ogaq Lake, Baffin Island, core 91-2b, 73.5 cm. The sediment surface is toward the *top* of the photo. Scale bar is 100 μm (Photograph: K. Hughen)

by a freshwater cap from continual stream input (Hughen et al. 1996a). Dense, hypersaline bottom waters can also form from dissolution of exposed salt formations on the seafloor, as is found in the Orca Basin, Gulf of Mexico (Kennett et al. 1985). Although not absolutely required for varve formation, anoxic bottom waters are one of the best indicators of potentially laminated sediments and are often used to help guide coring expeditions. For example, anoxic bottom waters occur where the oxygen minimum zone intersects the seafloor on the continental slopes, and annually laminated sediments have been located and studied off the coast of Pakistan (Schultz et al. 1998) as well as California (Anderson et al. 1987) and Peru (De Vries and Schrader 1981).

Classification and Morphology

For convenience, varves can be classified into basic types according to the most prominent seasonal feature or layer components. The earliest recognized and most commonly studied varved sediments are *clastic varves*, composed primarily of allochthonous mineral grains that differ seasonally in grain size (De Geer 1912; O'Sullivan 1983; Saarnisto 1986). Clastic varves are common in glacial marine and lacustrine settings where mineral grain production and deposition rates are high, and biological productivity is low. A magnified image of clastic varves from an Arctic lake (Fig. 1) illustrates typical sedimentary structures and fabric in this type of varve. The sediments consist of couplets of a light-colored, coarser-grained layer covered by a thin dark layer. Grains as large as fine sand mark the bottom of the coarse layer and grade upward into silt-sized particles, whereas a dark layer of fine clays caps the top of each couplet (Moore et al. 2001). The silts grade gradually upward into the fine clays, but the boundary between the clays and the overlying coarse grains is typically sharp (Fig. 1).

The succession of fine sands to silts in a thick layer, topped by a thin clay cap, is the classic structure of glacial varves (De Geer 1912; O'Sullivan 1983; Saarnisto 1986; Leeman and Niessen 1994; Zolitschka 1996; Retelle and Child 1996; Moore et al. 2001). The upward gradation from relatively coarse to fine grains in the thick layer results from a decrease in the energy available for sediment transport over the course of the summer. During the spring meltwater freshet, runoff is at a maximum and sands and silts previously locked up in winter ice are first available to be transported. Glacial runoff continues throughout the summer, but with snow cover mostly melted, the flux of runoff and energy of transport are diminished, and the size of grains washed into the basin is reduced (Retelle and Child 1996). During winter in glacial environments, surface water freezes and transport of sediment is greatly reduced or ceases altogether. In the absence of continual mixing, fine, clay-sized particles suspended in the water column settle out and form an independent dark clay layer. This idealized sequence can be interrupted by abrupt events such as intense rainstorms during the late summer or fall (Retelle and Child 1996; Lamoureux 1999). An increased pulse of runoff from a rainstorm can result in a sub-lamina of larger grains, often recognizable as an anomalous sand lens. The most diagnostic part of the sediment fabric is the clay cap, usually used to distinguish consecutive years' accumulation.

Another widely studied type of varved sediments are termed *biogenic* (O'Sullivan 1983; Saarnisto 1986) or *biochemical varves* (Lotter 1991). Biogenic varves form due to distinct pulses of aquatic biological productivity, including seasonal plankton blooms. The biological layer may interrupt and temporarily dilute a more constant rate of background deposition, such as mineral grains from steady stream flow or eolian input, or else alternate with a different distinct pulse of sedimentation, for example, mineral grains from monsoonal river runoff. A magnified image of biogenic varves from a coastal Arctic tidewater lake illustrates an example of these seasonal layers (Fig. 2). The biogenic layers form during the ice-free summer months, and during the winter, suspended particles settle out of the frozen, low-energy environment and are deposited as dark-colored, clay-rich layers (Hughen et al. 1996a, 2000a). Biogenic laminae form in a variety of marine and lacustrine environments, and in many cases a succession of distinct sub-laminae can be deposited as different diatom species bloom throughout the growth season (Dean et al. 1999).

Varves may also form through seasonal changes in the physical and chemical properties of the water column and are usually restricted to lakes. *Calcareous varves* may form in lakes with high CO_3^{2-} content, when calcite layers precipitate out of solution during summer warming (O'Sullivan 1983; Lotter 1991). *Ferrogenic varves* may form due to changes in redox conditions affecting the solubility of Fe species and the formation of sulfides versus hydroxides throughout the year (O'Sullivan 1983). *Evaporite varves* may form as interbedded laminae of precipitates in shallow evaporite basins and can consist of couplets of calcite and anhydrite (e.g., Castile Formation; Anderson and Dean 1995) or aragonite with eolian grains (e.g., Lake Lisan; Katz and Kologny 1989), depending on water chemistry.

Analytical Techniques

Independent Dating and Age Control

Before laminated sediments can be counted and used to construct calendar-age chronologies, it must be demonstrated using independent dating techniques that the laminae couplets are indeed annually deposited varves. Simply identifying and counting laminae couplets can lead to misinterpretation of event deposits as seasonal layers, or the counting of layers representing seasonal processes, but ones that do not occur on a regular basis from year to year. Numerous studies have used independent dating techniques to demonstrate that supposed "varves" were not in fact annually deposited (e.g., Crusius and Anderson 1992). Whenever possible, a combination of

several dating methods, such as lead-210 and anthropogenic nuclides, should be used both to increase confidence and to provide temporal coverage over a broader range of time scales.

Chronology Construction

By their nature, varves are a result of changing sediment supply to a depositional basin and should be present and recognizable throughout that basin. Subtle disturbances may disrupt or distort the varve sequence recovered in single sediment cores, however, and numerous steps are necessary to create a reliable annual chronology from laminated sediments. In constructing a varve chronology, many of the principles used in dendrochronology must be applied. For example, multiple measurements of varves (tree rings) from a single core (tree) must be averaged, followed by cross-correlation and averaging between multiple cores to build a chronology representative of an entire sediment basin (stand of trees). Small fluctuations in varve thickness as seen in thin sections require that each lamination be measured several times and averaged to provide an objective, representative record from each sediment core (Zolitschka 1996). In addition, local disturbances such as turbidites and erosional scours, as well as core breaks or gaps arising from the sampling process, may limit the physical integrity of a record from any single sediment core. To minimize these sources of error, it is critical to correlate varve chronologies constructed from multiple different cores and produce a basin-wide average (Zolitschka 1996; Hughen et al. 2000a). Downcore patterns of variation in varve thickness are usually quite distinct and can be recognized in cores across a basin. Cross-correlation of these marker patterns allow the identification and bridging of missing or disturbed sections in single cores. A larger number of cores used for cross-correlation increases the likelihood of avoiding all core gaps and constructing an accurate and reliable varve chronology.

Varve Applications

Geochronology

The geochronological applications of varved sediments are too numerous to provide an exhaustive list. One significant application that should be emphasized is the calibration and development of other geochronological tools, specifically, calibration of the radiocarbon time scale. Varves from lakes and marine basins have been one of the primary tools used to provide calendar-age calibration of ^{14}C ages beyond the limit of tree rings, >12,000 years ago (Hughen et al. 2000b; Ramsey et al. 2012). Annual calendar-age varve chronologies also provide accurate dates for specific sedimentological events, as well as age models for continuous sediment time series. An example of a study investigating discrete events would be paleoseismology. Earthquakes cause turbidity flows and turbidite deposits that in the proper setting can be dated by counting overlying varves (Hughen et al. 1996b). Interbedded sequences of varved sediments and massive turbidites can be used to determine recurrence intervals of earthquakes in a specific region (Blais-Stevens et al. 1997).

Varve chronologies offer an excellent means for constructing age models for high-resolution paleoclimate records. Varves are well suited to studies comparing the relative timing and lead-lag relationships of rapid climate changes in different regions, based on high-resolution paleoclimate records with calendar-age chronologies from varved sediments, tree rings, and ice cores (Hughen et al. 2000b). In addition, varve chronologies provide excellent precision at the annual scale and are particularly well suited for studies involving spectral analysis at short (sub-decadal) periodicities (Rittenour et al. 2000).

Applications Other Than Dating

In addition to having geochronological applications, varved sediments may themselves contain valuable paleoenvironmental information. For example, hydrological and sedimentological process studies in glacier-fed lakes have shown that the fluxes of runoff and suspended sediment, as well as varve thickness, vary logarithmically as a function of average temperature during the snow or glacier melting season (Leeman and Neissen 1994; Retelle and Child 1996). Downcore records of clastic varve or clastic laminae thickness from both glacial and non-glacial lakes correlate well with average summer or snowmelt season temperatures (Leeman and Neissen 1994; Hardy et al. 1996; Wohlfarth et al. 1998; Hughen et al. 2000a; Moore et al. 2001). For use as a paleotemperature proxy, it is critical that the varve thickness signal in any new location is calibrated for the recent period using instrumental data from a nearby meteorological station.

Varves have also been used to reconstruct changes in other paleoenvironmental parameters. Biogenic laminae in marine upwelling regimes reflect primary productivity and therefore the intensity of upwelling and trade winds, in the tropical North Atlantic during the last deglaciation (Hughen et al. 1996c). Laminated sediments, and their absence, have been used to reconstruct the ventilation history of intermediate-depth waters off the coast of California (Behl and Kennett 1996), Pakistan (Schultz et al. 1998) and northern South America (Peterson et al. 2000). These studies and others have shown that abrupt climatic shifts first seen in the high latitude North Atlantic region were in fact global in scope. Finally, varves can be used to study changes in past glacial activity and evolution of sediment source regions, as well as evolution of sedimentary basins (Lamoureux 1999). The applications of varved sediments to geochronological and paleoenvironmental research are limitless and will continue to grow as increasingly sophisticated methods are developed for obtaining and analyzing them.

Conclusions

Annually laminated (varved) sediments are valuable tools for research in geochronology, as well as other disciplines including paleoclimatology, paleoseismology, and archeology. Varved sediments are formed when distinct layers of sediment are deposited during different seasons throughout the year and occur in a wide variety of environments all over the globe. They are found in diverse settings from alpine glaciers and coastal tidewater lakes to isolated marine basins and continental slopes and occur at all latitudes from the high Arctic to the tropics. Varves can be counted and measured, similar to tree rings, in order to provide accurate calendar-age chronologies. Varve chronologies can be used in geochronological research in order to study and develop sediment dating techniques, such as ^{210}Pb and ^{14}C , and to date single events such as earthquakes and turbidity currents. Varves can also be applied to the reconstruction of past environmental conditions. At a minimum, varves provide annual-resolution calendar-age models for records based on other climate proxies (stable isotopes, pollen, etc.). In the best cases, however, varves themselves can be shown to contain environmental information and thus combine high temporal precision and accuracy with paleoenvironmental reconstructions from the same archive.

Cross-References

- [C Dating](#)
- [Pb Dating](#)

- [Evaporitic Varves](#)
- [Geochronology](#)
- [Lacustrine Varves](#)
- [Varve Chronology](#)

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Meteorites (^{36}Cl)

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Definition

Cosmogenic nuclide: A stable or radioactive isotope that is produced by the interaction of terrestrial or extraterrestrial materials with galactic and/or solar cosmic rays.

Meteorites: An extraterrestrial rock or iron that survived passage through the atmosphere and landed on Earth. Most meteorites are pieces of collisional debris from asteroids or comets, although a small percentage are fragments of the moon and Mars.

Introduction

Cosmogenic nuclides provide information on a meteorite's history, specifically during their travel through space as meter-sized objects, in which they were exposed to cosmic rays. More than 50 different cosmogenic nuclides have been detected in meteorites, including the stable isotopes of the noble gases, He, Ne, Ar, Kr, and Xe, and radioactive nuclides with half-lives ranging from less than 1 day (^{24}Na) to 1.28 Ga (^{40}K). The measured concentrations of cosmogenic nuclides in meteorites provide information on the total exposure time of meteorites to cosmic rays, also known as the cosmic-ray exposure (CRE) age. Since cosmic rays penetrate about 1 m deep, the CRE age represents the time since a meteorite was ejected as a meter-sized object from its parent body, although a few meteorites show evidence of CRE on the surface of their parent body. The most commonly measured nuclides in meteorites are listed in Table 1, along with their production mechanism and the analytical method used to measure each nuclide. Although most cosmogenic nuclides are mainly produced by interactions with galactic cosmic rays (GCR), a few of the nuclides (including ^{22}Na , ^{22}Ne , ^{26}Al , ^{54}Mn , and ^{56}Co) are also produced by solar cosmic rays (SCR). However, since the SCR flux is dominated by particles with energies <100 MeV, SCR contributions are only expected in the outer few cm of a meteoroid, which is usually lost during atmospheric passage. Therefore, SCR effects are rarely observed in meteorites.

In addition, the cosmogenic radionuclides (such as ^{14}C , ^{41}Ca , ^{36}Cl , and ^{81}Kr) also provide information on the terrestrial age of a meteorite, the time elapsed since it fell on Earth and was shielded from the high cosmic ray flux it experienced in space. Terrestrial ages of meteorites are especially interesting for meteorites from hot deserts (e.g., Australia, Southwestern USA, Sahara, Atacama, and the Arabian Peninsula) and from Antarctica. In addition, the terrestrial age of a meteorite find is needed to calculate the ejection age, i.e., the time a meteorite was ejected from its parent body, which equals the sum of the CRE age and the terrestrial age. For most meteorites, the terrestrial age is small compared to the cosmic-ray exposure age, but for lunar meteorites and certain carbonaceous chondrites, both ages have to be taken into account.

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Table 1 Cosmogenic nuclides produced in meteorites

Nuclide	$t_{1/2}$ (year)	Major target elements	Main production mechanism	Method of analysis
^{54}Mn	0.855	Fe, Ni	Spallation	γ -ray spectrometry
^{22}Na	2.61	Mg, Si	Spallation	γ -ray spectrometry
^{60}Co	5.27	Co	$^{59}\text{Co}(n, \gamma)$	γ -ray spectrometry
^{14}C	5.730	O, Mg, Si	Spallation	AMS
^{59}Ni	7.6×10^4	Fe, Ni	Spallation, $^{58}\text{Ni}(n, \gamma)$	AMS
^{41}Ca	1.04×10^5	Fe, Ca	Spallation, $^{40}\text{Ca}(n, \gamma)$	AMS
^{81}Kr	2.29×10^5	Rb, Sr, Y, Zr	Spallation	Noble gas MS
^{36}Cl	3.01×10^5	K, Ca, Ti, Fe, Cl	Spallation, $^{36}\text{Cl}(n, \gamma)$	AMS
^{26}Al	7.05×10^5	Si, Al, Mg, (Fe)	Spallation	AMS, γ -ray spectrometry
^{10}Be	1.36×10^6	O, Mg, Si, (Fe)	Spallation	AMS
^{53}Mn	3.7×10^6	Fe, Ni	Spallation	AMS, INAA
^{129}I	1.57×10^7	Te, Ba, La	Spallation, $^{128}\text{Te}(n, \gamma)$	AMS
^{40}K	1.28×10^9	Fe, Ni	Spallation	
^3He	Stable	O, Mg, Si, Fe	Spallation	Noble gas MS
^{20}Ne , ^{21}Ne , ^{22}Ne	Stable	Mg, Al, Si	GCR	Noble gas MS
^{36}Ar , ^{38}Ar	Stable	Ca, Fe	GCR	Noble gas MS
$^{78, 80, 82, 83, 84}\text{Kr}$	Stable	Rb, Sr, Y, Zr, Nb	Spallation, $^{79}\text{Br}(n, \gamma)$ ^{80}Kr , $^{81}\text{Br}(n, \gamma)$ ^{82}Kr	Noble gas MS
$^{126-136}\text{Xe}$	Stable	Ba, REE	Spallation	Noble gas MS

N_{th} : thermal neutron capture

Analytical Methods

Cosmogenic noble gases are measured using a noble gas mass spectrometer. Samples of 10–500 mg are usually wrapped in a metal (Al, Ni) foil and stored under vacuum in one of several storage arms that are connected to the mass spectrometer. After preheating the samples at 100–120 °C to remove absorbed atmospheric gases, the cosmogenic (as well as radiogenic and trapped) noble gases are extracted by heating the sample in a furnace for 15–30 min at 1,750–1,800 °C. The noble gases are then separated and purified, and their abundance and isotopic composition are measured in a mass spectrometer with a Nier-type ion source (Begemann et al. 1976; Signer et al. 1977). Using known ratios for the cosmogenic and trapped noble gases, the individual contributions of cosmogenic and trapped He, Ne, Ar, Kr, and Xe are calculated (e.g., Eugster 1988).

Short-lived cosmogenic radionuclides as well as ^{26}Al are measured by gamma-ray spectrometry (Evans et al. 1982). This method requires samples of 5–100 g and is nondestructive, but generally requires counting times of several days to several weeks. Long-lived cosmogenic radionuclides (including ^{14}C , ^{10}Be , ^{26}Al , ^{36}Cl , ^{41}Ca , ^{53}Mn , ^{59}Ni , ^{60}Fe , and ^{129}I) are measured by accelerator mass spectrometry (AMS). For this method, samples of ~100 mg are dissolved in the presence of known carrier amounts of the stable nuclide of each element of interest. After dissolution, a small aliquot of the sample is taken for chemical analysis, and each cosmogenic nuclide is separated by ion exchange and solvent extraction techniques. The isotopic ratio of the radioactive to the stable isotope is measured by AMS, and the concentration of the radionuclide (in atoms per gram meteorite) is calculated from the measured isotope ratio, the amount of carrier added, and the sample mass. Radionuclide concentrations in meteorites are generally reported in decay rates, i.e., disintegrations

per minute per kg (dpm/kg). Since most meteorites were exposed to cosmic rays in space long enough ($>10^7$ years) to reach saturation levels for radionuclides with half-lives up to a few Ma, the measured activities generally also represent the production rates (in atoms per minute per kg).

Cosmic-Ray Exposure Age Methods

Many different methods have been used to determine the CRE ages of meteorites (e.g., Herzog 2005). Some exposure age methods can only be applied for iron meteorites (and the metal phase of stony irons), while others only apply to stone meteorites. Production rates of cosmogenic nuclides in meteorites depend on their chemical composition, the size of meteoroid during irradiation in space, and depth of the samples within the meteoroid. The size and depth effects are generally lumped together under the term “shielding,” reflecting the attenuation of primary cosmic ray particles as well as the buildup of secondary particles (protons and neutrons). Since meteorites typically lose 50–99 % of their pre-atmospheric mass during atmospheric passage (breakup and ablation processes), the original size and pre-atmospheric depth of individual meteorites are not known and can only be estimated from the measured cosmogenic nuclide concentrations or cosmic-ray track densities. Many empirical relationships between different cosmogenic nuclides have been established that help in calculating absolute production rates in individual samples and thus to obtain shielding-corrected CRE ages.

In general, the most reliable CRE age methods are the ones that combine a stable nuclide (e.g., ^{36}Ar , ^{21}Ne , ^{83}Kr) and a radionuclide (e.g., ^{10}Be , ^{26}Al , ^{36}Cl , ^{81}Kr). In these methods, the radionuclide (if it has reached saturation level) serves as an internal shielding parameter, which can be used to calibrate the production rate of the stable nuclide. However, many exposure ages of stony meteorites, which generally come from objects of less than 1 m in diameter, are based on noble gas concentrations only, in combination with the $^{22}\text{Ne}/^{21}\text{Ne}$ ratio, which serves as a shielding parameter for objects <1 m in diameter.

Noble Gas Exposure Ages of Stony Meteorites

The majority of CRE ages of stony meteorites are based on the concentrations of cosmogenic ^3He , ^{21}Ne , and ^{38}Ar (Marti and Graf 1992; Graf and Marti 1994, 1995; Eugster and Michel 1995; Welten et al. 1997; Scherer et al. 1998; Scherer and Schultz 2000; Rai et al. 2003). The concentration of cosmogenic ^{21}Ne is generally considered the most reliable of the three nuclides, since ^3He is more susceptible to diffusion losses and ^{38}Ar is more sensitive to variations in chemical composition (mainly Ca, Fe). In some achondrites, including howardites and eucrites, the ^{38}Ar ages are more reliable than ^3He and ^{21}Ne , as the production of ^{38}Ar is higher due to the high Ca concentrations, while ^3He and ^{21}Ne suffer diffusive losses (mainly from plagioclase).

The production rates of ^3He , ^{21}Ne , and ^{38}Ar are generally derived from empirical relationships with the $^{22}\text{Ne}/^{21}\text{Ne}$ ratio, which serves as a shielding indicator and generally ranges from 1.05 at high shielding to 1.25 at low shielding. The relationship between ^{21}Ne and the $^{22}\text{Ne}/^{21}\text{Ne}$ ratio in chondrites was first established by Eberhardt et al. (1966) and was later refined by Herzog and Anders (1971a), Nishiizumi et al. (1980), and Eugster (1988). The most commonly used equation for the ^{21}Ne production rate, $P(^{21}\text{Ne})$, expressed in 10^{-8} cm³ STP/g/Ma, in chondrites is

$$P(^{21}\text{Ne}) = 1.61 * F21 / \left[21.77 * \left(^{22}\text{Ne}/^{21}\text{Ne} \right) - 19.32 \right], \quad (1)$$

in which F_{21} is the chemical correction factor for different types of chondrites and the term in the denominator serves as shielding correction.

Similar empirical relationships were proposed for the production rates of ^3He , ^{38}Ar , ^{83}Kr , and ^{126}Xe in chondrites (Eugster 1988) as well as for noble gas production rates in achondrites (Eugster and Michel 1995). Model calculations have shown that the simple relationships between production rates and the $^{22}\text{Ne}/^{21}\text{Ne}$ ratio are generally valid for chondritic objects <1 m in diameter, which dominate the meteoroid flux to Earth. However, these simple relationships fail for larger objects, for which they result in overestimation of the production rates (Graf et al. 1990b; Masarik et al. 2001; Welten et al. 2003; Leya and Masarik 2009). For larger objects, it is recommended to use exposure age methods which are based on the combination of a stable nuclide and a radionuclide with similar production mechanisms. We will discuss the most commonly used methods for stony and iron meteorites.

The ^{81}Kr –Kr Method

Cosmogenic Kr in stony meteorites is mainly produced from the trace elements Rb, Sr, Y, Zr, and Nb. Although the concentration of cosmogenic Kr is several orders of magnitude lower than for cosmogenic He, Ne, and Ar, cosmogenic Kr was first detected in lunar samples (Marti 1967) and later in many meteorites, including achondrites and chondrites (Eugster et al. 1967; Finkel et al. 1978; Freundel et al. 1986; Lavielle and Marti 1988; Eugster 1988). The ^{81}Kr –Kr method is based on the combination of stable Kr isotopes, mainly ^{78}Kr , ^{80}Kr , ^{82}Kr , and ^{83}Kr , and the radioactive isotope ^{81}Kr , which reaches saturation after ~ 1.5 Ma of exposure. To determine the CRE age of a meteorite, one has to know the $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ ratio, which is shielding dependent. There are generally two ways to derive this ratio, i.e., by using the empirical relationship between $^{81}\text{Kr}/^{83}\text{Kr}$ and $^{78}\text{Kr}/^{83}\text{Kr}$ ratio derived from Apollo 12 samples (Eq. 2) (Marti and Lugmair 1971) or the theoretical relationship for Kr production by spallation (Eq. 3), in which the $^{81}\text{Kr}/^{83}\text{Kr}$ production ratio is determined from the measured $^{80}\text{Kr}/^{83}\text{Kr}$ and $^{82}\text{Kr}/^{83}\text{Kr}$ ratios assuming an isobaric fraction yield of 0.95 (Marti 1967):

$$P(^{81}\text{Kr})/P(^{83}\text{Kr}) = 1.262 * ^{78}\text{Kr}/^{83}\text{Kr} + 0.381 \quad (2)$$

$$P(^{81}\text{Kr})/P(^{83}\text{Kr}) = 0.95 * \left(^{80}\text{Kr}/^{83}\text{Kr} + ^{82}\text{Kr}/^{83}\text{Kr} \right) / 2 \quad (3)$$

The latter approach has the advantage that it is less dependent on variations in chemical composition of different meteorites, but its disadvantage is that in large meteorites, ^{80}Kr and ^{82}Kr are not only produced by spallation reactions but also by neutron-capture reactions on ^{79}Br and ^{81}Br , respectively, thus leading to an overestimation of the $P(^{81}\text{Kr})/P(^{83}\text{Kr})$ values. Therefore, Eq. 2, which uses the $^{78}\text{Kr}/^{83}\text{Kr}$ ratio as shielding indicator, is more widely applicable and thus has been used for many different types of meteorites (e.g., Eugster et al. 1967; Finkel et al. 1978; Freundel et al. 1986; Lavielle and Marti 1988; Eugster 1988; Shukolyukov and Begemann 1996; Leya et al. 2004). Since the relatively small cosmogenic Kr contributions have to be determined from a mixture of cosmogenic and trapped Kr components, the ^{81}Kr –Kr method is most reliable for meteorites with long exposure ages (>10 Ma), high concentrations of target elements (e.g., howardites, eucrites), and low concentrations of trapped Kr (either planetary or terrestrial). The latter condition is valid for equilibrated chondrites and achondrites and implies that observed falls are more suitable than weathered finds.

The ^{36}Cl – ^{36}Ar Method

The ^{36}Cl – ^{36}Ar technique is generally considered the most reliable dating method for iron meteorites (e.g., Lavielle et al. 1999) and the metal phase of stony irons (Begemann et al. 1976). The ^{36}Cl and ^{36}Ar are produced by spallation reactions on Fe and Ni (e.g., Begemann et al. 1976). Since the reaction mechanism of the two products is almost identical, the $^{36}\text{Cl}/^{36}\text{Ar}$ production rate ratio that is essentially independent from shielding conditions (Schaeffer and Heymann 1965; Lavielle et al. 1999). In addition, more than 98 % of the produced ^{36}Cl , which is in saturation after a few million years of cosmic-ray exposure, decays to ^{36}Ar . As a result, more than 80 % of the ^{36}Ar in the metal phase is from decay of the radionuclide ^{36}Cl (half-life = 3.01×10^5 year). Since ^{36}Cl and ^{36}Ar concentrations can be determined accurately and are relatively insensitive to silicate contamination, typical uncertainties in the ^{36}Cl – ^{36}Ar ages are 3–5 % (Lavielle et al. 1999; Graf et al. 2001). For calculating ^{36}Cl – ^{36}Ar exposure ages, T^{36} (in Ma), the following equation can be used (Lavielle et al. 1999; Leya and Masarik 2009):

$$T^{36} = 511 * P(^{36}\text{Cl})/P(^{36}\text{Ar}) * [^{36}\text{Ar}]/[^{36}\text{Cl}] + 0.36, \quad (4)$$

in which $[^{36}\text{Ar}]$ and $[^{36}\text{Cl}]$ are the measured concentrations of cosmogenic ^{36}Ar [in units of $10^{-8} \text{ cm}^3 \text{ STP g}^{-1}$] and ^{36}Cl (in dpm kg^{-1}) in metal and $P(^{36}\text{Cl})/P(^{36}\text{Ar}) = 0.835 \pm 0.040$ atom/atom (Lavielle et al. 1999). The additional constant (of 0.36 Ma) takes into account that – at the time of the meteorite fall – some of the cosmogenic ^{36}Cl has not yet decayed to ^{36}Ar (Leya and Masarik 2009). The ^{36}Cl – ^{36}Ar method is most reliable if the measured ^{36}Cl concentration represents the saturation value, i.e., for meteorites with CRE ages >2 Ma and short terrestrial ages, although corrections can be made for radioactive decay of ^{36}Cl during the terrestrial residence time if the terrestrial age is known (Lavielle et al. 1999). The ^{36}Cl – ^{36}Ar method has also been applied to the metal phases of stony irons (Begemann et al. 1976; Albrecht et al. 2000; Honda et al. 2002) and the metal phase of stone meteorites (Graf et al. 2001; Leya et al. 2001).

The ^{26}Al – ^{21}Ne Method

Iron meteorites. The energy dependence of ^{26}Al and ^{21}Ne production from spallation reactions on Fe (and Ni) is very similar, which makes the $^{26}\text{Al}/^{21}\text{Ne}$ ratio in metal insensitive to variations in shielding and thus suitable for determining CRE ages of iron meteorites. Lipschutz et al. (1965) calculated CRE ages of iron meteorites from the measured $^{26}\text{Al}/^{21}\text{Ne}$ ratio, in which ^{26}Al and ^{21}Ne concentrations are expressed in dpm/kg and $10^{-8} \text{ cm}^3 \text{ STP/g}$, respectively. Using Eq. 5, assuming a constant $^{26}\text{Al}/^{21}\text{Ne}$ production rate ratio of 0.37 (atom/atom), while later studies used slightly different ratios of 0.38 (Hampel and Schaeffer 1979; Lavielle et al. 1999) and 0.35 (Honda et al. 2002).

$$T(^{26}\text{Al} - ^{21}\text{Ne}) = 511 * P(^{26}\text{Al})/P(^{21}\text{Ne}) * [^{21}\text{Ne}]/[^{26}\text{Al}] \quad (5)$$

The ^{26}Al – ^{21}Ne ages of 17 iron meteorites of different pre-atmospheric size (Lavielle et al. 1999) and of 8 metal separates from a wide range of shielding depths in the large Brenham stony iron meteorite (Honda et al. 2002) generally yield good agreement (within ~ 10 %) with the corresponding ^{36}Cl – ^{36}Ar ages. Although the $^{26}\text{Al}/^{21}\text{Ne}$ method is reliable for most iron meteorites and the metal phase of stony irons, it has not been applied to the metal phase of chondritic meteorites due to large contributions of ^{26}Al and ^{21}Ne from silicates, which are difficult to remove from the chondritic metal phase. However, for chondrites and other stone meteorites, the $^{26}\text{Al}/^{21}\text{Ne}$ method can also be applied to bulk samples, albeit with a different production ratio.

Stony meteorites. The production mechanisms of ^{26}Al and ^{21}Ne in stony meteorites are dominated by low-energy reactions on Al + Si (for ^{26}Al) and Mg, Al, and Si (for ^{21}Ne). One therefore expects that the production rates of ^{26}Al and ^{21}Ne in stone meteorites show very similar dependence on shielding conditions (Herzog and Anders 1971b). The constancy of the $^{26}\text{Al}/^{21}\text{Ne}$ ratio in chondrites has been investigated by several empirical and semiempirical studies (e.g., Graf et al. 1990a, b; Nagai et al. 1993; Honda et al. 2002; Welten et al. 2003) as well as by model calculations (Leya et al. 2001; Leya and Masarik 2009). Although the shielding dependence of the $^{26}\text{Al}/^{21}\text{Ne}$ ratio varies slightly among different studies, a relatively constant $^{26}\text{Al}/^{21}\text{Ne}$ production ratio of 0.35–0.42 atom/atom seems consistent with most studies. This method has been used to calculate CRE ages for several large chondrites (e.g., Leya et al. 2001; Welten et al. 2001, 2003), for which the CRE age cannot be calculated from cosmogenic Ne data alone.

The ^{10}Be – ^{21}Ne Method

Iron meteorites. Cross-section data for the production of ^{10}Be and ^{21}Ne from high-energy proton reactions on Fe suggest that the production ratio of $^{10}\text{Be}/^{21}\text{Ne}$ in irons does not show a significant depth dependency, which is confirmed by relatively constant $^{10}\text{Be}/^{21}\text{Ne}$ ratios measured in samples from different shielding depths in two iron meteorites (Graf et al. 1987; Lavielle et al. 1999) and in metal phases of the Brenham stony iron (Honda et al. 2002). Therefore, Eq. 6 can be used to calculate the CRE ages from the measured $^{21}\text{Ne}/^{10}\text{Be}$ ratios in iron meteorites

$$T = 511 * P(^{10}\text{Be})/P(^{21}\text{Ne}) * [^{21}\text{Ne}]/[^{10}\text{Be}] \quad (6)$$

in which $[^{21}\text{Ne}]$ and $[^{10}\text{Be}]$ are the measured concentrations of ^{21}Ne [in $10^{-8} \text{ cm}^3 \text{ STP g}^{-1}$] and of ^{10}Be (in dpm kg^{-1}) in metal. For the $P(^{10}\text{Be})/P(^{21}\text{Ne})$ ratio, values of 0.55 (Lavielle et al. 1999) and 0.50 atom/atom (Honda et al. 2002) have been used. The latter study found that the $^{10}\text{Be}/^{21}\text{Ne}$ ages of metal phases in the Brenham pallasite agree with the ^{36}Cl – ^{36}Ar ages, while absolute production rates varied by three orders of magnitude. Despite empirical evidence that the $^{10}\text{Be}/^{21}\text{Ne}$ ratio in iron meteorites is remarkably constant, Ammon et al. (2009) caution against using the $^{10}\text{Be}/^{21}\text{Ne}$ ratio for CRE ages of iron meteorites, since their model calculations indicate that trace elements (such as P and S) can affect the $^{10}\text{Be}/^{21}\text{Ne}$ production ratio.

Stony meteorites. Depth profiles of ^{10}Be and ^{21}Ne in the large Knyahinya chondrite indicate that the $^{10}\text{Be}/^{21}\text{Ne}$ ratio in a meter-sized object is relatively constant even though concentrations of both nuclides increase by more than 20 % from the surface to the center of the meteorite (Graf et al. 1990a). The semiempirical model of Graf et al. (1990b) suggests that the $^{10}\text{Be}/^{21}\text{Ne}$ ratio is relatively constant at 0.14 atom/atom, although it may show small variations (5–10 %) as a function of shielding. Subsequent model calculations based on particle fluxes and proton and neutron cross sections (Leya et al. 2000; Leya and Masarik 2009) suggest that the $^{10}\text{Be}/^{21}\text{Ne}$ production ratio is more sensitive to shielding than in the semiempirical model of Graf and is probably lower for high shielding conditions. This conclusion is also confirmed by empirical studies, which suggest production ratios of 0.10–0.12 atom/atom for high shielding (Leya et al. 2001; Welten et al. 2004). Although the exact relationship between the $^{10}\text{Be}/^{21}\text{Ne}$ ratio and shielding is still a topic of ongoing research, and the $^{10}\text{Be}/^{21}\text{Ne}$ ratio thus has an uncertainty of $\sim 20\%$, the $^{10}\text{Be}/^{21}\text{Ne}$ method is already more reliable for very large meteorites, such as the Gold Basin meteorite (Welten et al. 2003), for which the simple relationship between ^{21}Ne production rate and $^{22}\text{Ne}/^{21}\text{Ne}$ ratio fails.

Terrestrial Age Methods

Cosmogenic radionuclide concentrations also provide information on the terrestrial ages of meteorite finds. The method that is most suitable for terrestrial age determination of a meteorite depends on the metal content of the meteorite (metal rich vs. metal poor), its find location, and its expected terrestrial age. We will discuss the most commonly used methods below.

^{14}C and $^{14}\text{C}/^{10}\text{Be}$ Terrestrial Ages

The terrestrial ages of stony meteorites that fell less than 30–40 ka ago can best be determined by measuring the cosmogenic ^{14}C concentration of finds relative to falls. Since 99 % of cosmogenic ^{14}C in stony meteorites is produced from oxygen, the ^{14}C production rate is simply a function of bulk O content, which is generally well known and does not vary more than 20–30 % among different types of stone meteorites. Measurements of ^{14}C in observed falls suggest saturation values of 30–60 dpm/kg for chondrites with radii of <50 cm (Jull et al. 1989; Wieler et al. 1996), which is valid for more than 90 % of all stony meteorites. For average-size meteorites (<1 m in diameter), a constant production rate, $P(^{14}\text{C})$, is generally assumed, leading to the following equation for the terrestrial age, $T(^{14}\text{C})$, in which T is expressed in ka and $P(^{14}\text{C})$ and $A(^{14}\text{C})$ in dpm/kg:

$$T(^{14}\text{C}) = 8.27 * \ln[P(^{14}\text{C})/A(^{14}\text{C})] \quad (7)$$

This method was first applied to meteorite finds from the Southwestern USA (Boeckl 1972), revealing terrestrial ages up to ~13 ka. With the introduction of ^{14}C AMS measurements, the required sample size was reduced to <1 g. The method was applied to meteorites from other hot deserts (Jull et al. 1990; Bland et al. 1998) as well as Antarctica (Jull et al. 1989).

However, the assumption of an average production rate of 45–50 dpm/kg is not valid for very large meteorites, as was shown for the Gold Basin chondrite shower (Kring et al. 2001). In very large meteorites, the terrestrial age is best determined by measuring the ratio of $^{14}\text{C}/^{10}\text{Be}$, which is relatively insensitive to shielding effects and is assumed to be constant at ~2.5 in chondrite falls. This method is valid on the condition that the meteorite had a minimum CRE of 5–7 Ma, i.e., long enough to saturate both ^{14}C and ^{10}Be , or that the CRE age is well known, so that corrections for undersaturation of ^{10}Be can be made. Kring et al. (2001) showed that the measured $^{14}\text{C}/^{10}\text{Be}$ ratio in fragments of the large Gold Basin meteorite is relatively constant, even though absolute ^{14}C and ^{10}Be concentrations varied by more than a factor of 10 due to differences in shielding depth. Comparison of ^{14}C ages with shielding-corrected ^{14}C – ^{10}Be ages for a set of meteorites from the Nullarbor desert in Australia shows that the two ages generally agree within 1–2 ka, which is the typical uncertainty in the ^{14}C method (Jull et al. 2010). For meteorites older than 30–40 ka, the ^{14}C method only provides a lower limit, and measurements of longer-lived radionuclides, such as ^{41}Ca , ^{36}Cl , ^{26}Al , or ^{81}Kr , are needed to further constrain the terrestrial age (Nishiizumi et al. 1989; Welten et al. 2004, 2006, 2008).

^{36}Cl and $^{36}\text{Cl}/^{10}\text{Be}$ Terrestrial Ages

For Antarctic meteorites, which have typical terrestrial ages of 10 ka to ~1 Ma, the radionuclide ^{36}Cl is most suitable for terrestrial age determinations due to its half-life of 0.3 Ma and the relatively constant ^{36}Cl production rate of 20–25 dpm/kg in small irons and the metal phase of most chondrites (Nishiizumi et al. 1989). The terrestrial age (in ka) can then be calculated from the following equation:

$$T(^{36}\text{Cl}) = 434 * \ln[P(^{36}\text{Cl})/A(^{36}\text{Cl})] \quad (8)$$

in which $P(^{36}\text{Cl})$ is generally assumed to be 22.1 ± 2.8 dpm kg^{-1} (Nishiizumi 1995), leading to typical 2σ uncertainties of ~ 55 ka in the terrestrial age.

As with most other cosmogenic nuclide methods for meteorites, this simple approach is not valid for large iron meteorites (Chang and Wänke 1969; Nishiizumi et al. 1987; Lavielle et al. 1999) or large chondrite showers, such as Queen Alexandra Range 90201 (Welten et al. 2011). A more reliable terrestrial age method for iron meteorites, which often show large variations in shielding and large chondrites, is based on the $^{36}\text{Cl}/^{10}\text{Be}$ ratio. Although this ratio was initially assumed to be constant at ~ 4.3 (Chang and Wänke 1969), additional measurements have shown that the ratio increases systematically from ~ 3.5 in small irons to ~ 6 in large irons (Lavielle et al. 1999). The $^{36}\text{Cl}/^{10}\text{Be}$ saturation ratio shows a strong correlation with the ^{10}Be concentration in the metal phase, yielding the following equation:

$$[^{36}\text{Cl}/^{10}\text{Be}] = 5.97 - 0.184 * [^{10}\text{Be}] - 0.024 * [^{10}\text{Be}]^2 \quad (9)$$

This equation was later updated with the three constants as 6.01, 0.28, and 0.009, respectively (Welten et al. 2006), in which the ^{10}Be saturation value ranges from 0 to ~ 7 dpm/kg. The 2σ uncertainty in the $^{36}\text{Cl}/^{10}\text{Be}$ ratio is estimated to be $\sim 6\%$, corresponding to an uncertainty of ~ 35 ka in the shielding-corrected terrestrial age. The terrestrial age (in ka) is calculated from the measured $^{36}\text{Cl}/^{10}\text{Be}$ ratio and ^{10}Be concentrations in a few iterative steps, in which the $^{36}\text{Cl}/^{10}\text{Be}$ saturation value is recalculated in each step from the decay-corrected ^{10}Be concentration:

$$T(^{36}\text{Cl}/^{10}\text{Be}) = 557 * \ln \left[\left(^{36}\text{Cl}/^{10}\text{Be} \right)_{\text{sat}} / \left(^{36}\text{Cl}/^{10}\text{Be} \right)_m \right] \quad (10)$$

This method is straightforward for iron meteorites for which both ^{36}Cl and ^{10}Be are generally saturated at the time of fall, since they have CRE ages > 50 Ma. For the metal phase of chondrites, sometimes a small correction has to be made for undersaturation of the ^{10}Be concentration if the CRE age is < 10 Ma (Welten et al. 2006, 2011).

^{41}Ca and $^{41}\text{Ca}/^{36}\text{Cl}$ Terrestrial Ages

The production mechanism of ^{41}Ca is similar to that of ^{36}Cl , i.e., it is mainly produced by spallation from Fe. The average saturation value of ^{41}Ca in small iron meteorites is 24 ± 1 dpm/kg (Fink et al. 1991), i.e., slightly higher than the average ^{36}Cl value of 22.1 ± 1.4 dpm/kg. Although it was initially assumed that the $^{41}\text{Ca}/^{36}\text{Cl}$ ratio is relatively constant at 1.0–1.1 (Fink et al. 1991; Klein et al. 1991), additional measurements in larger iron meteorites and the metal phases of stony irons and chondrites have shown that the ratio exhibits a small shielding dependence (Nishiizumi and Caffee 1998). This shielding dependence is also confirmed by model calculations (Leya and Masarik 2009). The shielding dependence of the $^{41}\text{Ca}/^{36}\text{Cl}$ ratio is best described by the following empirical relationship with the ^{36}Cl concentration (Welten et al. 2006, 2011):

$$[^{41}\text{Ca}/^{36}\text{Cl}] = 1.25 + 0.003 * [^{36}\text{Cl}] - 0.0006 * [^{36}\text{Cl}]^2 \quad (11)$$

in which the ^{41}Ca and ^{36}Cl concentrations in the metal fraction are expressed in dpm kg^{-1} .

The terrestrial age (in ka), $T(^{41}\text{Ca}/^{36}\text{Cl})$, is then calculated from the measured $^{41}\text{Ca}/^{36}\text{Cl}$ ratio and ^{36}Cl concentration, using equation 12. The $^{41}\text{Ca}/^{36}\text{Cl}$ saturation value is calculated in a few iterative steps using Eq. 11 and the decay-corrected ^{36}Cl concentration until the terrestrial age changes less than 0.1 ka:

$$T(^{41}\text{Ca}/^{36}\text{Cl}) = 229 * \ln \left[\left(^{41}\text{Ca}/^{36}\text{Cl} \right)_{\text{sat}} / \left(^{41}\text{Ca}/^{36}\text{Cl} \right)_{\text{m}} \right] \quad (12)$$

^{81}Kr – Kr Terrestrial Ages

Terrestrial ages >40 ka are more difficult to determine for achondrites, which usually have very little (if any) metal, therefore hampering the determination of ^{36}Cl or ^{41}Ca ages from the metal phase. For meteorites with high plagioclase contents, such as eucrites, the combination of radioactive ^{81}Kr with stable ^{83}Kr provides a good alternative for terrestrial age determinations. In this method, the measured $^{81}\text{Kr}/^{83}\text{Kr}$ ratio is both a function of the CRE age (as described above) and of radioactive decay of ^{81}Kr during the terrestrial residence time (Freundel et al. 1986). If the CRE age of the meteorite is well known from independent measurements (such as cosmogenic ^{38}Ar), then the $^{81}\text{Kr}/^{83}\text{Kr}$ ratio provides a measure of the terrestrial age. This method is most suitable for ages of 100–600 ka and has been applied to Antarctic eucrites (Freundel et al. 1986) as well as for a few achondrites from hot deserts (Nishiizumi et al. 2002).

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Bivalve Sclerochronology

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Synonyms

Bivalve shell chronometer; Related to dendrochronology

Definition

Sclerochronology: The study of incremental growth patterns in hard part remains of organisms that grow by accretion (i.e., adding on discrete growth layers throughout the life of the organism). The term “sclerochronology” was introduced for the study of growth patterns in calcareous exoskeletons or shells and applied to study the rate and patterns of coral growth (Buddemeier et al. 1974). It is analogous to the earlier established approach of dendrochronology. The application of the term “sclerochronology” has since broadened to the hard parts of many other aquatic taxa (e.g., bivalves, limpets, fish, and coralline sponges).

Bivalve: Bivalves are in the class Bivalvia of the phylum Mollusca and include freshwater, marine, and estuarine clams, mussels, quahogs, scallops, and oysters. They have a wide biogeographic distribution, extending from the equator to the poles, and occur from shallow to deep water. Furthermore, bivalves have a long geologic history and are archaeologically important. Fossil bivalves document more than 500 million years of evolutionary history. Bivalves from archaeological deposits (e.g., shell middens) provide information on food-gathering activities of historic and prehistoric people and insights into human-climate interactions. Many taxa are relatively short-lived (e.g., *Mercenaria* spp., *Spisula* spp., *Chione*, spp., *Crassostrea virginica*); however, many other bivalve species are extremely long-lived (e.g., *Arctica islandica*, *Neopycnodonte zibrowii*, and *Margaritifera margaritifera*). Their shells are composed of calcium carbonate (CaCO₃), most commonly in the form of aragonite and/or calcite. The ultrahigh-resolution (daily, seasonal, annual) records of growth increments enable bivalve shells to serve as unique skeletal diaries.

Introduction

Many hard part remains of aquatic organisms form by accretionary growth, implying that the accretion of new material is periodically retarded or interrupted which results in the formation of growth lines. Growth lines delimit growth increments, i.e., periods of fast growth. Growth increments represent time slices on annual, fortnightly (tidal), circadian (24-h cycle), circalunidian (lunar day; on average, 24 h and 50 min), and ultradian (period shorter than a day, minutes to hours) scales. Together, growth lines and increments can be used to estimate ontogenetic age and season

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of growth and add a calendar date to discrete shell portions. Biological clocks entrained by environmental pacemakers (e.g., light/dark cycles, tidal cycles, food availability) apparently control the regular formation of growth lines and increments. This entry focuses on the use of sclerochronology in bivalve shells.

Bivalve sclerochronology can provide environmental and ecological data from many different spatial, temporal, and cultural settings. Combining sclerochronology with geochemical analyses (e.g., oxygen and carbon isotope ratios; $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values, respectively) can provide additional environmental and ecological information, such as water temperature, precipitation, glacial melt-water pulses, primary productivity, etc. The key criterion for chronological research, however, is precise time control. The following section provides an overview on the formation of periodic growth patterns in bivalves and focuses on daily, fortnightly, and annual increments. We refer the reader to Schöne and Surge (2012) for a more detailed discussion of bivalve sclerochronology and geochemistry.

Shell Growth Patterns

Shell growth patterns result from changes in the rate of deposition associated with variations in chemical composition and crystallographic properties. Growth lines separate the growth pattern into time slices referred to as growth increments. Together, growth lines and increments form a shell calendar, providing an ideal method to measure time. They are typically studied in the outer or middle shell layers of cross-sectioned valves cut along the maximum axis of growth. Several methods, such as staining and acetate peels, have been developed to visualize growth patterns (Clark 1980; Kennish et al. 1980; Tevez and Carter 1980; Richardson 1987; Schöne et al. 2005a).

The outer shell layer and portions of the middle shell layer provide a complete and undisturbed shell record, assuming no diagenesis or taphonomic alteration. New shell material is deposited along the shell margins including inner surfaces when the shell is open (gaping). Shell dissolution may occur along the inner shell layer and portions of the middle shell layer when the valves are closed for extended periods of time (e.g., during seasonal anoxia, beyond temperature or salinity tolerances) (Crenshaw 1980). Therefore, these portions of the shell should be avoided for calendar-dated studies. The outer shell layer and outer portion of the middle layer are not affected by dissolution during shell closure.

Many bivalve shells contain daily microgrowth increments, which are ideally studied in fast-growing, young portions of the shells. Under optimal growth conditions, some pectinids and giant clams (*Tridacna* spp.) form increments corresponding to the number of solar days that elapsed during that growth interval (Clark 1974, 1975; Parsons et al. 1993; Watanabe and Oba 1999; Chauvaud et al. 2005). This finding suggests that such microgrowth increments form with circadian periodicity (Clark 1975).

Some bivalves from intertidal habitats produce distinct, tidally controlled growth patterns in their shells. Growth cessation occurs when they are aerially exposed during low tide and resumes during high tide when they are submerged (House and Farrow 1968; Evans 1972; Ohno 1989; Goodwin et al. 2001; Miyaji et al. 2007). It should be noted, however, that most bivalves form circalunidian increments regardless of whether or not they are aerially exposed at low tide. Under semidiurnal tidal conditions, two growth lines and increments (two circatidal growth patterns) can form per lunar day. Growth lines produced during spring tides are more prominent than those formed during neap tides. The distance from the shoreline influences the duration of aerial exposure and, hence, the number of growth lines and increments. For example, bivalves living in

the high intertidal zone can be exposed for several days during extreme spring tides without forming growth lines and increments. In comparison, individuals farther away from the shoreline are submerged for longer intervals and can have significantly more growth lines and increments relative to specimens from the high intertidal zone (Ohno 1989). Moreover, shells from the low intertidal zones typically have broader growth increments than shells from mid-intertidal settings. This pattern is influenced by the duration of submergence. Similarly, shorter submergence times during spring tides produce narrow growth increments relative to wider increments formed during neap tides. Tidally influenced lines and increments form distinct bundles of ~13–15. Schöne and Surge (2012) provide a more detailed explanation about the mechanisms controlling daily and semidiurnal shell growth.

Most bivalve species produce annual growth lines or increments in their shells (Hall et al. 1974; Jones 1980; Brey and Mackensen 1997). Prominent dark growth lines or increments are often visible with the naked eye on the outer shell surface or in cross section along the maximum axis of growth. Under high magnification, annual growth increments appear as bundles of closely spaced daily growth lines (Barker 1964; Hall et al. 1974). Daily growth lines gradually decrease in width (i.e., growth slows) toward annual growth lines and increase gradually afterward as growth rates increase. This important feature distinguishes annual growth lines from disturbance lines. Disturbance lines are characterized by abruptly changing microgrowth increment widths and can occur when the animal is exposed to a sudden environmental stress, such as a major storm. Some species (e.g., *Mercenaria mercenaria*, *M. campechiensis*, *Spisula solidissima*) form couplets of dark and light increments visible under reflected light (translucent and opaque under transmitted light), which together represents 1 year of growth (Lutz and Rhoads 1980; Jones 1983; Peterson et al. 1983; Jones et al. 1990; Arnold et al. 1998). Dark/translucent increments occur during periods of slow growth, whereas light/opaque increments form during fast growth intervals (Jones 1983; Jones et al. 1990). It should be noted that not all bivalve species produce obvious periodic growth lines or increments. Surge et al. (2001) reported that annual cycles in shells of the American oyster, *Crassostrea virginica*, are only apparent through stable isotope analysis (see, however, Kirby et al. 1998).

Possible mechanisms that produce annual growth line formation include reproductive processes (i.e., gonad development and spawning), food supply, and minimum or maximum temperature thresholds (Pannella and MacClintock 1968; Lutz and Rhoads 1977; Jones 1980, 1983; Jones et al. 1990; Cerrato et al. 1991; Jones and Quitmyer 1996; Brockington and Clarke 2001; Surge et al. 2001; Schöne et al. 2005b; García-March et al. 2011). Thermal tolerance is an important control for annual growth line/increment formation in many shallow-water mollusks (e.g., Kraeuter and Castagna 2001 and references therein; Beukema et al. 1985; Brown 1988; Tanabe and Oba 1988; Schöne et al. 2003b; Surge et al. 2013). In their seminal paper on isotope sclerochronology, Jones and Quitmyer (1996) reported that the timing of slow growth (dark/translucent increments) in *Mercenaria mercenaria* and *M. campechiensis* shells from the east coast of North America and Gulf of Mexico occurs during cold winter temperature in mid latitudes (cold-temperate zone), whereas specimens from low latitudes (warm-temperate zone) slow their shell growth during summer (see, however, Elliot et al. 2002; Henry and Cerrato 2007). They noted that at the transition between the warm- and cold-temperate zones, both winter and summer growth increments are present. Despite the importance of thermal tolerance on shell growth rates, the formation of annual growth lines/increments is probably a function of a combination of environmental factors, physiology, and endogenous rhythms (Brockington and Clarke 2001). In many cases the underlying reason for annual growth formation remains obscure. For example, at different latitudes of the North Atlantic, the ocean quahog, *A. islandica*, spawns at different times of the year or even year-

round (Thórarinsdóttir 2000), and the reproductive cycles of different populations are not synchronized (Fritz 1991). Yet, according to $\delta^{18}\text{O}$ data, annual growth lines always form about a month after the seasonal temperature maximum (Weidman et al. 1994; Witbaard et al. 1994; Schöne et al. 2005b, c). It appears likely that circadian/circalunidian biological clocks are used to measure time that elapsed after the summer temperature peak in order to determine the timing of seasonal growth retardation.

Applications of Shell Growth Pattern Analysis

Sclerochronology offers a wide range of potential applications in a variety of disciplines, such as biology, ecology, archaeology, and climate research. Here we provide examples of selected applications.

Two approaches have been used to estimate the timing, duration, and rate of seasonal shell growth. The translucent-opaque staging technique identifies the stage of terminal growth as being within either the translucent (dark) increment or the opaque (light) increment on a cross-sectioned valve cut along the maximum axis of growth (Jones et al. 1990; Arnold et al. 1998). Next, the growth phase is determined within each stage of terminal growth based on the relative thickness of the terminal growth band (Quitmyer and Jones 1992, 2012; Quitmyer et al. 1997; Arnold et al. 1998; Quitmyer 2013). Another approach counts the number of daily growth lines between annual increments to estimate the duration of the growing season and assign precise dates to each shell portion (assuming the date of the last-formed growth line is known). This method is potentially accurate to the nearest 2–4 weeks (Hallmann et al. 2009). If maximum and minimum temperature thresholds of a species are known, such data can be used to determine changes in seasonal temperature variability and climate through time and space (Ansell 1968; Tanabe and Oba 1988; Jones and Quitmyer 1996; Schöne et al. 2004; Lohmann and Schöne 2013).

When combined with oxygen and carbon isotope ratios (discussed more fully in the next section), isotope sclerochronology can be used to address ecological questions in modern and fossil shells to interpret life history and to assess the timing of the initial introduction of invasive species (Jones and Quitmyer 1996; Schöne et al. 2002; Henry and Cerrato 2007; Goodwin et al. 2010; Haveles and Ivany 2010). For example, it was recently discovered that bivalves are among the longest-lived solitary animals with some species living for many centuries (Thompson et al. 1980; Shaul and Goodwin 1982; Mutvei and Westermarck 2001; Schöne et al. 2005b; Wanamaker et al. 2008; Wisshak et al. 2009; Butler et al. 2013). Such long-lived species have been used to generate master chronologies for long-term climate reconstruction (Noakes and Campbell 1992; Marchitto et al. 2000; Schöne et al. 2003a; Strom et al. 2004, 2005; Wanamaker et al. 2008; Butler et al. 2010, 2013). Paleoclimate, paleoceanographic, and paleoenvironmental reconstruction based on isotope sclerochronology provides critical information on seasonality in seawater temperature, North Atlantic Oscillation (NAO) variability, paleoproductivity/upwelling, drought conditions, changes in river discharge, and aquatic pollution (Schöne et al. 2003b, 2005b; Dettman et al. 2004; Dunca et al. 2005; Carroll et al. 2009; Schöne and Fiebig 2009; Harding et al. 2010; Wanamaker et al. 2011; Wang et al. 2011; Sadler et al. 2012). Sclerochronologic analysis of shells from archaeological midden deposits (trash heaps) allows interpretation of human activity, such as site occupation, season of harvest, and intensification of resource exploitation (Bailey et al. 1983; Milner 2001; Milner et al. 2007; Carré et al. 2009; Andrus 2011; Gutiérrez-Zugasti 2011; Andrus and Thompson 2012; Reitz et al. 2012 and references therein; Burchell et al., 2013a, b).

Isotope Sclerochronology

Stable carbon isotope ratios of bivalve shells are reported in delta notation:

$$\delta^{13}\text{C}_{\text{shell}} = \left(\frac{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{shell}} - \frac{^{13}\text{C}}{^{12}\text{C}}_{\text{VPDB}}}{\frac{^{13}\text{C}}{^{12}\text{C}}_{\text{VPDB}}} \right) \cdot 1,000$$

where VPDB is the Vienna Pee Dee Belemnite standard and values are in per mil units (‰). In principle, $\delta^{13}\text{C}_{\text{shell}}$ values can provide information on the carbon isotope ratio of dissolved inorganic carbon (DIC) and, hence, serve as a proxy for primary productivity and remineralization (e.g., respiration, oxidation of organic matter) (Mook and Vogel 1968). Plants preferentially incorporate ^{12}C in their organic tissue, thereby enriching the remaining carbon pool in ^{13}C . Thus, increases in photosynthesis results in higher $\delta^{13}\text{C}_{\text{DIC}}$ values, whereas increased respiration lowers $\delta^{13}\text{C}_{\text{DIC}}$ values. Bivalves sample the carbon isotope ratio of the ambient water and in theory record changes in the $\delta^{13}\text{C}$ value of DIC. For example, higher $\delta^{13}\text{C}_{\text{shell}}$ values would reflect increased primary productivity, whereas lower $\delta^{13}\text{C}_{\text{shell}}$ values suggest increased respiration. However, bivalves also incorporate up to ca. 10 % metabolically derived CO_2 into their shells (McConnaughey and Gillikin 2008). Many species seem to incorporate increased amounts of respiratory CO_2 through their lifetime, resulting in more negative $\delta^{13}\text{C}_{\text{shell}}$ values as the animal ages (Gillikin et al. 2007; McConnaughey and Gillikin 2008). Therefore, $\delta^{13}\text{C}_{\text{shell}}$ values should be treated with caution. More recent studies have reported that long-lived bivalves that grow slowly during their youth are not hampered by such ontogenetic effects on the carbon isotope ratio of shell carbonate. In these cases, studying past carbon cycle dynamics in the ocean or tracking the anthropogenic increase in atmospheric and oceanic CO_2 (i.e., the Suess effect) is possible (Butler et al. 2011; Schöne et al. 2011).

Unlike stable carbon isotope ratios, metabolic effects (also known as vital effects) do not seem to impact oxygen isotope ratios recorded in bivalve shells. Oxygen isotope ratios are reported in similar delta notation as stable carbon isotope ratios:

$$\delta^{18}\text{O}_{\text{shell}} = \left(\frac{\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{shell}} - \frac{^{18}\text{O}}{^{16}\text{O}}_{\text{VPDB}}}{\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{VPDB}}} \right) \cdot 1,000$$

They are the most widely used geochemical proxy of bivalve shells and are a function of variations in the ambient water temperature and $\delta^{18}\text{O}_{\text{water}}$ value (Urey 1947; Epstein et al. 1953). Many studies have demonstrated that almost all bivalves precipitate their shells in oxygen isotopic equilibrium with the ambient water (Mook and Vogel 1968; Surge et al. 2001; Elliot et al. 2003; Hallmann et al. 2009; see, however, Owen et al. 2002, 2008; Hallmann et al. 2008; Yan et al. 2012). Values of $\delta^{18}\text{O}_{\text{shell}}$ have been used to estimate salinity (assuming temperature can be held constant and the mixing relation between marine and freshwater is known; Ingram et al. 1996) or water temperature (assuming the $\delta^{18}\text{O}_{\text{water}}$ value can be held constant; Jones et al. 1989; Wefer and Berger 1991; Weidman et al. 1994; Dettman et al. 1999; Surge et al. 2001; Carré et al. 2005; Schöne et al. 2005b, c; Wanamaker et al. 2006; Ivany et al. 2008). Several experimental studies have demonstrated a 1 ‰ change in $\delta^{18}\text{O}_{\text{shell}}$ value that represents a temperature change of ~4.3 °C (Epstein et al. 1953; Grossman and Ku 1986; Dettman et al. 1999). Higher $\delta^{18}\text{O}_{\text{shell}}$ values

correspond to cold temperatures, whereas relatively lower values indicate warmer temperatures. Advances in microsampling techniques enable high-resolution isotopic records that can produce temperature reconstructions on seasonal to subdaily time scales, depending on shell growth rates, to the nearest 0.35 °C (Dettman and Lohmann 1995). Sclerochronologic analysis ensures that the reconstructed temperature record from $\delta^{18}\text{O}_{\text{shell}}$ values is placed within a precise temporal context.

Other geochemical proxies in bivalve shells used to reconstruct environmental conditions with varying degrees of success include clumped isotopes, nitrogen isotopes, and minor and trace elemental ratios. We refer the reader to Schöne and Surge (2012) and Schöne and Gillikin (2013) (and papers therein) for more details and examples regarding these topics.

Summary

Bivalve sclerochronology developed from the observations of visible growth lines and increments on the outer shell layer and along cross-sectioned shells cut along the maximum axis of growth. Such growth patterns are often visible with the naked eye, but in some species these features are more clearly revealed with staining or acetate peels. Sclerochronologic records from long-lived bivalves provide master chronologies used to reconstruct climate change on decadal to centennial time scales. Records from short-lived bivalves can be resolved on seasonal time scales. In combination with geochemical proxies, sclerochronologic records can produce time series of environmental variability that can be quantified (e.g., estimating water temperature, salinity). Their abundance in fossil and archaeological deposits and their wide biogeographic distribution make bivalve shells unique and valuable archives for a wide range of interdisciplinary study.

Cross-References

- Corals (Sclerochronology) Dendrochronology, Paleoclimate
- Molluscs, Foraminifera, and Other Carbonate Fossils
- Otolith

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Peat (^{14}C)

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Definition

Peat. A highly organic soil that results when waterlogged anaerobic conditions suppress the degradation of vegetation.

Radiocarbon dating of peat. Measurement of the radiocarbon content in samples of either bulk peat or carbon-bearing fractions isolated from bulk peat by physical and/or chemical treatments. The objective is usually either to provide an absolute chronology for environmental or archaeological records contained within a peat deposit or to understand the biogeochemical cycling of carbon within the peat system.

Introduction

Peat is a highly organic deposit (e.g., 50–95 % organic matter on a dry mass basis), comprising a thin, more rapidly cycling “acrotelm” layer, overlying a thick, saturated “catotelm” layer, in which vegetation decay is very slow (Ingram 1978; Clymo 1984). Peat develops as a result of waterlogged anaerobic and acidic conditions that inhibit vegetation decomposition (c.f. Yavitt and Lang 1990; Johnson and Damman 1991; Valentine et al. 1994; Maltby and Proctor 1996; Bridgham et al. 1998). When the rate of net primary production at the peat surface exceeds losses from decomposition, the peat deposit grows in depth and/or extent. Peatlands (also termed “bogs,” “mires,” “fens,” or “swamps”) are hence commonly located on low-gradient slopes where glacial deposits or bedrock impede drainage (Rabassa et al. 1996; Coronato et al. 2006). Peat growth is an important form of carbon storage; although peatlands cover around 3 % of the Earth’s land area, they contain 20–30 % of the global soil carbon (C) pool, storing an estimated 270–450 Pg (1 Pg = 10^{15} g) of C, equivalent to c. 50 % of C in atmospheric CO_2 (Gorham 1991; Turunen et al. 2002; Zoltai and Martikainen 1996; Moore et al. 1998; Limpens et al. 2008). Carbon inputs in peat include C fixed via photosynthesis from atmospheric CO_2 or dissolved carbon and C delivered to the peat from atmospheric deposition, surface runoff, or groundwater flow. Peat is also a source of carbon, as anaerobic decomposition releases methane (CH_4) to the atmosphere (Wang et al. 2004), and water transport from peatlands carries dissolved organic carbon to the oceans (Hope et al. 1994).

Bulk peat can be described as a “heterogeneous mix of organic matter of different origins and different ages in varying stages of biological degradation and humification” (Brock et al. 2011, p. 550), meaning that radiocarbon dating of this material presents a range of practical and theoretical problems and should be approached with care in order to obtain accurate and precise results. Radiocarbon dating of peat and its subfractions is desirable however, as this material forms a valuable long-term archive of environmental and archaeological data extending over timescales of up to 10^5 and even 10^6 years. Material held within the peat deposit, as well as the peat itself, can serve as a proxy for environmental conditions (e.g., temperature, precipitation, volcanic activity, fire

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histories) at the time of deposition. Examples of proxies studied from peat include macrofossils (e.g., Barber et al. 2003), geochemical parameters (e.g., Shotyk 1996), atmospheric cations/particulates (e.g., Clymo et al. 1990), pollen (e.g., Edwards 1979) and charcoal (e.g., Ohlson et al. 2006). In addition, peat deposits frequently contain archaeological material, including structural (e.g., Coles and Coles 1986) and human remains (e.g., Stead et al. 1986). Ongoing decomposition and compaction within peat deposits, coupled with varying accumulation rates through time, mean that depth is generally not linearly related to age within a peat deposit (Clymo 1984; Clymo et al. 1990) and absolute dating methods are required to construct a reliable timescale upon which to place proxy records obtained from peat and compare between records (c.f. Blaauw and Christen 2005). The variations in net peat accumulation rates through time that are identified through radiocarbon dating also provide a useful climatic proxy in themselves, as accumulation rates vary as a response to past climate change (e.g., Mauquoy et al. 2008).

In addition to being an environmental/archaeological archive, peatlands form a key component of the global carbon cycle, and ^{14}C is also used as a tracer to investigate the biogeochemical cycling of carbon within the peat system. Understanding peatland carbon dynamics is particularly important in the light of potential future climatic change, which is likely to be pronounced at higher latitudes, where peat deposits are concentrated. This is achieved through analysis of specific chemical fractions in peat to quantify their turnover/transport rates and residence times within peatlands. Examples include ^{14}C measurement of gases and dissolved organic carbon released from peatland sample sites (Billett et al. 2007; Tipping et al. 2010; Garnett et al. 2011).

Sampling and Pretreatment of Peat for ^{14}C Dating

Prior to radiocarbon measurement, peat samples must undergo laboratory pretreatment. The aim of the pretreatment process is to isolate material of interest for dating from contaminating carbon that has a different ^{14}C age. The first step in radiocarbon dating of peat involves the selection of a suitable section of peat, obtained from a deposit in the field. The aim of sampling peat for ^{14}C dating is to select the sample that is most representative of the age of the peat layer itself. Larger samples may be subdivided in the laboratory, depending upon the chronological resolution required. To date the peat itself, initial processing (c.f. Harkness et al. 1989) involves air-drying, followed by sieving (typically <3 mm) to remove large root fragments (which may represent intrusive material of a different age to the peat itself), and finally the sample is homogenized by grinding. At this stage, it is possible to obtain a ^{14}C measurement on the sample. Several studies have, however, raised doubts over the reliability of dates obtained on bulk peat (Kilian et al. 1995; Shore et al. 1995; Nilsson et al. 2001), and in practice it is more common to extract specific chemical fractions from peat for dating. Radiocarbon dating laboratories consequently usually separate peat into three operationally defined fractions for dating on the basis of pH-dependent solubility. These are humin (acid and alkali insoluble), humic acids (alkali soluble, acid insoluble), and fulvic acids (acid and alkali soluble) (Cook et al. 1998). Humic and fulvic acids are a product of the humification processes that occur as decomposing vegetation is transformed into peat, while humin is the fraction most representative of the original plant material that was converted to peat. Isolation of fulvic acids is performed in order to remove this fraction from the humic acids and humin and discard it. This is because the acid solubility of fulvic acids renders them mobile in the peat profile, meaning they are unreliable for dating (Shore et al. 1995). Conversely, humic acids and humin are thought to provide ^{14}C ages that more accurately reflect the time at which the peat sample formed. Pretreatment to isolate humic acids involves an acid wash, followed by an alkali wash, to extract both humic and fulvic acids. The

extract is filtered to isolate solids (i.e., the humin fraction) and then acidified to precipitate the humic acids (e.g., Brock et al. 2010). Fulvic acids remain in solution and can be discarded. Precise procedures used vary between laboratories, with differences between factors such as acid/alkali concentrations, extraction duration, and number of extractions (Cook et al. 1998). Along with peat itself, intact organic remains contained within the peat may be obtained for dating, most commonly plant macrofossils or charcoal fragments. The usual process for dating such material is firstly isolation from the bulk peat matrix by handpicking or wet-sieving. Isolated plant material or charcoal is then subjected to an acid–base–acid pretreatment (e.g., Hatté et al. 2001) to remove contaminating carbon, where removal of fulvic and humic acids by alkali extraction is followed by a final acid wash to remove any contamination added through the absorption of atmospheric CO₂ during alkali treatment.

Considerations to Maximize Accuracy and Precision of ¹⁴C Dates on Peat

Peat presents difficulties when applying the ¹⁴C method, particularly when the aim of the work is to date the time since a specific layer in the peat was formed. For the date to be accurate, the carbon that is dated must solely represent this formation event. Bulk peat is hence thought unreliable for ¹⁴C dating because it contains a variable mix of material of different ages (including aboveground biomass, roots, fungi, insect remains, diatoms, spores, pollen, charred vegetation, etc.) (Blaauw et al. 2004a; Brock et al. 2011), and any radiocarbon age will therefore simply be an integration of the ages of these substances, weighted by mass in the sample, rather than reflecting an actual date of deposition/final formation for a peat horizon. However, multiple studies show that the humic acid and humin fractions in peat can differ substantially in age and radiocarbon content (Stout et al. 1981; Hammond et al. 1991; Shore et al. 1995), raising questions over which fraction is most suitable for dating. Whichever fraction is selected, the accuracy of radiocarbon dates on peat is improved by minimizing the possibility that the sample contains contaminating carbon. Contamination can be introduced either while the peat deposit is in situ or following sampling. Contamination introduced in situ includes modern roots and rhizomes penetrating into the peat from above (Saarinen 1996) and the movement of dissolved organic carbon (including humic acids) through the peat profile (Nilsson et al. 2001; Turetsky et al. 2004). Care should be taken to identify the possibility that physical movement through frost-heaving has not disturbed the peat profile and buried surface peat with older deposits.

Another factor to consider is the possibility of whether peat samples are affected by radiocarbon reservoir effects. A ¹⁴C reservoir effect is a ¹⁴C age offset between a particular carbon reservoir versus the atmosphere at any particular point in time. This means that samples grown or formed in the affected reservoir will have a ¹⁴C age that is offset from their “true” atmospheric ¹⁴C age. Radiocarbon reservoir effects typically result from the introduction of “pre-aged” carbon into a reservoir, such as carbon derived from dissolution of geological carbonates, also known as the “hard-water” effect (Shotton 1972). Aquatic mosses in peat have been found to have a reservoir effect due to uptake of ¹⁴C-depleted carbon during growth (MacDonald et al. 1987), meaning that macrofossils or vegetation selected from peat for radiocarbon dating should be restricted to species that solely obtain carbon from atmospheric CO₂ (Turetsky et al. 2004). Other potential sources of old carbon include in-washing of ancient soil carbon to peat deposits via groundwater or overland flow (Edwards and Rowntree 1980) and organic matter released via thawing permafrost (Damon et al. 1996). Following sampling, as with any sedimentary or soil material, peat can be contaminated by the growth of vegetation or bacterial action during storage (e.g., Geyh et al. 1974). Appropriate

preventative measures include shortening storage time before analysis and storing samples cold, frozen, or dried prior to analysis.

Constructing Absolute Peat Chronologies: Calibration and Age–Depth Modeling Considerations

The radiocarbon method requires that the ^{14}C content of the sample at the time of measurement (A_s) is compared with the ^{14}C content of the sample when it was living (A_0). A primary standard material (currently Oxalic Acid II) is used to give a universal value for (A_0). This, however, assumes that the ^{14}C content of the atmosphere has been constant through time. In fact, fluctuations in atmospheric ^{14}C content due to reasons including variations in the Earth's magnetic field, fluctuating intensity of the solar wind, and human influence mean that radiocarbon ages must be calibrated to convert to the calendar timescale. For samples formed in equilibrium with the ^{14}C content of atmospheric CO_2 , the current curve is IntCal09 (Reimer et al. 2013). Calibration of ^{14}C ages in a peat deposit can be performed in conjunction with age–depth modeling to estimate the calendar age ranges of depths within the peat profile that lie between ^{14}C -dated layers (e.g., Blaauw et al. 2007; Bronk Ramsey 2008). Particular considerations are required when constructing ^{14}C -based chronologies in peat for periods after around AD 1650, due to large fluctuations in atmospheric ^{14}C content, due to both solar activity minima (the Maunder and Dalton events) and anthropogenically induced changes. The latter involve the reduction of atmospheric ^{14}C content due to release of ^{14}C -dead CO_2 from fossil fuel burning (also known as the Suess effect) and an elevation in atmospheric ^{14}C content due to detonation of nuclear weapons in the years up to AD 1963. With respect to the period after c. AD 1950, the bomb ^{14}C fluctuations can be used advantageously to achieve highly precise dates of peat deposits with uncertainties on the order of 1–2 years (e.g., Goodsite et al. 2001). For other periods where calibration is problematic due to atmospheric ^{14}C fluctuations, the technique of “wiggle-matching” can be used to obtain accurate chronologies (e.g., Blaauw et al. 2004b). Wiggle-matching relies on the premise that a time-ordered sequence of ^{14}C dates from a peat deposit should match the sequence represented in the ^{14}C calibration curve and can produce highly precise and accurate calibrated chronologies, particularly when combined with Bayesian statistics (e.g., Blaauw et al. 2007). Radiocarbon dating can also be usefully combined with other dating methods in order to reduce uncertainties and improve the robustness of age models. Such methods include ^{210}Pb dating (e.g., Clymo et al. 1990; Oldfield et al. 1997; Malmer and Wallén 1999; Loisel and Garneau 2010; Le Roux and Marshall 2011), chrono-stratigraphic markers from nuclear weapons testing, or the Chernobyl accident and tephrochronology (e.g., Dugmore et al. 2000).

Summary and Conclusions

Radiocarbon dating of peat presents particular problems, not least due to the chemically and physically heterogeneous nature of this material, potentially comprising a mix of carbon-containing compounds with ages spanning several thousand years. Despite this, ^{14}C dates on peat provide crucial chronological information for a key source of climatic, archaeological, and paleoenvironmental data. To obtain the best results, in which both precision and accuracy of ages are maximized, careful sample selection and chemical pretreatment are required, which should be combined with consideration of potential calibration issues. The application of statistical approaches, such as wiggle-matching combined with Bayesian analysis, is likely to improve

chronological resolution in instances where sufficient ^{14}C dates are performed on a profile, as is the combination of ^{14}C measurements with other dating methods.

Cross-References

- ▶ [14C Dating](#)
- ▶ [210Pb Dating](#)
- ▶ [Accelerator Mass Spectrometry](#)
- ▶ [Bomb Carbon](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Plant Materials \(14C\)](#)
- ▶ [Water \(14C\)](#)

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Category B: Planetary Surfaces (Cratering Rate)

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Synonyms

[Bombardment history](#); [Cratering statistics](#); [Projectile flux](#)

Definitions

Planetary surface: Interface between the solid (or liquid) material of a planet and either its atmosphere or the outer space. Actual planetary surfaces are found only on solid planetary bodies, such as the terrestrial planets, moons, or planetesimals.

Cratering rate: The rate at which craters of a given size form per time interval and surface unit.

Introduction

Planetary surfaces carry the imprint of geological evolution of the specific planetary body and, when dated, allow estimates of the timing and rates of geological processes. Establishment of the geological evolutionary history (chronostratigraphy) of solid-surface planetary bodies is based on the most common surface-modifying geological process, impact cratering. The crater density indicates a relative sequence of events, and when calibrated by radiometric dating of returned samples (e.g., Apollo samples from the Moon), crater density-based relative ages can be converted to absolute temporal information. This can allow dating of, for example, volcanic or structural events and frame the thermal evolution of a planetary body.

Cratering on Planetary Surfaces

Impact cratering occurs at all scales. Projectiles can range from micrometer-sized dust particles to planetesimals of 10s or even 100s of kilometers in size. Planets without atmosphere can record millimeter-sized craters to impact basins of 2,500 km width. One of the largest impact events during solar system evolution is probably the collision of a large planetesimal with proto-Earth that resulted in the Moon's formation (e.g., Canup 2004). Remnants of planetesimals of the planet-forming period are found in the asteroid main belt between Mars and Jupiter and beyond the orbit of Neptune. From these belts, objects can be moved into planet-crossing orbits due to gravitational resonant interaction and collisions or due to solar radiation pressure. These objects are the projectiles that have hit the terrestrial planets and the Moon.

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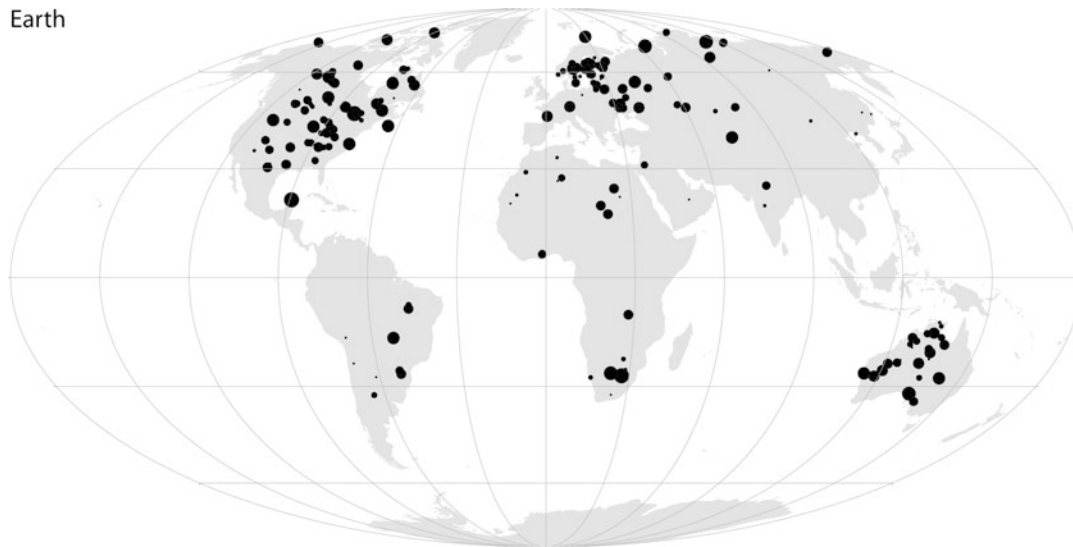


Fig. 1 Spatial impact crater distribution of all known craters on Earth (according to the Earth Impact Database, June 2013, <http://www.passc.net/EarthImpactDatabase/>). The craters are plotted with symbols representing gradually increasing crater sizes

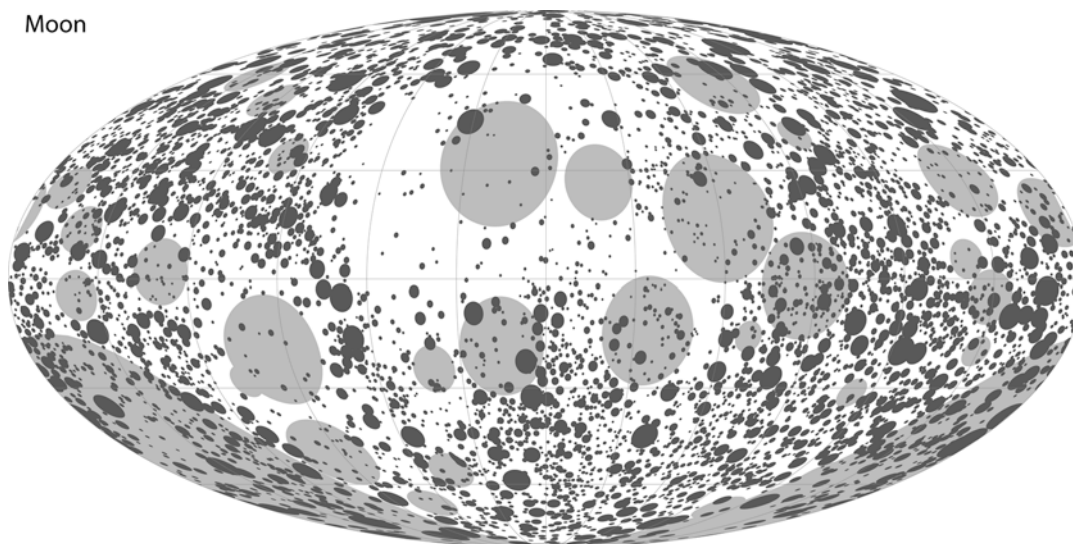


Fig. 2 Spatial impact crater distribution for the Moon (after Head et al. 2010). Craters larger than 20 km (*black*) and lunar basins larger than about 250 km (*gray*) in diameter are plotted to scale

On Earth, craters are almost exclusively found on continents, with slightly denser crater populations on the old cratonic units. Only few craters are detected on continental shelf units. No crater is so far confirmed for oceanic units. Craters are found on the seafloor with lower probability, because of the relative young age of oceanic crust, which is, on average, about 67 Ma old (calculated here according to Müller et al. 1997), and because of the strong shielding effect of the, on average, 5-km-deep water column. Figure 1 shows the total known crater record on Earth with crater diameters assigned by gradually changing symbol sizes for visibility. A very different picture of cratering history is preserved on the Moon (Fig. 2). The lack of a significant atmosphere, very old surface ages, as well as relatively limited endogenic geological activity suggest that the lunar cratering record was accumulated during nearly the entire evolution of the solar system.

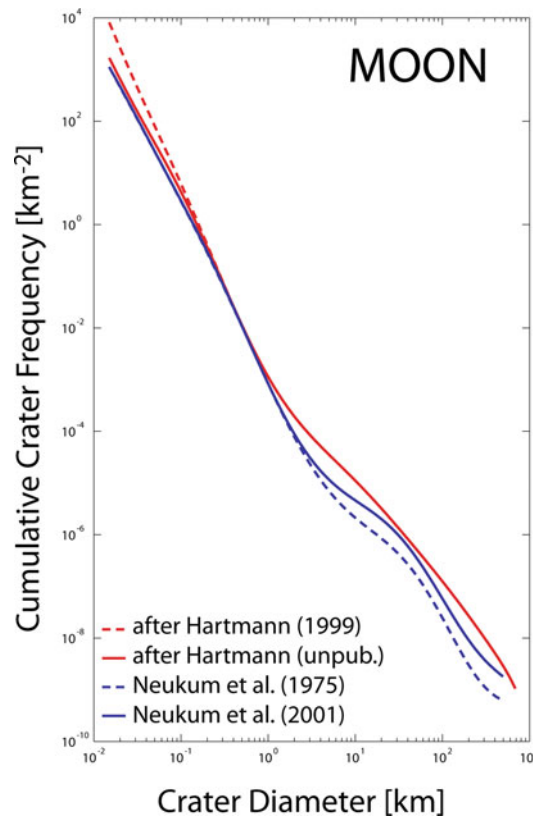


Fig. 3 Examples of four different but commonly used cumulative crater size–frequency distributions in log–log space, determined for the Moon

The oldest solid material found on the Moon has been dated at 4.47 Ga. Therefore, the lunar surface is commonly considered a good basis for calibration of cratering rates throughout solar system history. Additionally, the Moon is the only other planetary body (besides Earth) for which datable samples are available and that yielded ages determined in the laboratories on Earth using radiogenic isotopes.

Dating of cratered planetary surfaces requires combining the information from geological mapping and crater count statistics. Mapping delineates materials by geomorphological, multi-spectral, or reflectance features based on natural breaks in the rock sequence, while crater count statistics provide a quantitative tool for defining relative ages and absolute model ages (calibrated by isotope ages). The determination of absolute model ages on the Moon (and other solid-surface objects) is based on the application of a crater–production function (Fig. 3) and a cratering chronology model, which describes the integrated cratering rate through time (Fig. 4). The crater–production function describes the expected crater size–frequency distribution observed for a geological unit at a specific time and is, when scaled, similar for all planetary bodies (e.g., Ivanov et al. 2002).

For statistical evaluation and age determination, craters are recorded by their size and plotted into histograms, such as the crater size–frequency distribution curves. Graphs used to display crater statistics plot *cumulative* crater frequencies (number of craters greater than a given size per square kilometer, N_{cum}) against the crater diameter D on log–log plots. Distribution characteristics are defined by polynomial functions or multiple-segment power laws, where the cumulative frequency N_{cum} is proportional to D^{-b} and b varies between 4 and 1.5 (e.g., Hartmann 1999; Neukum et al. 2001, Fig. 3). There are other representations, such as *incremental* or *relative* (R) plots. The latter

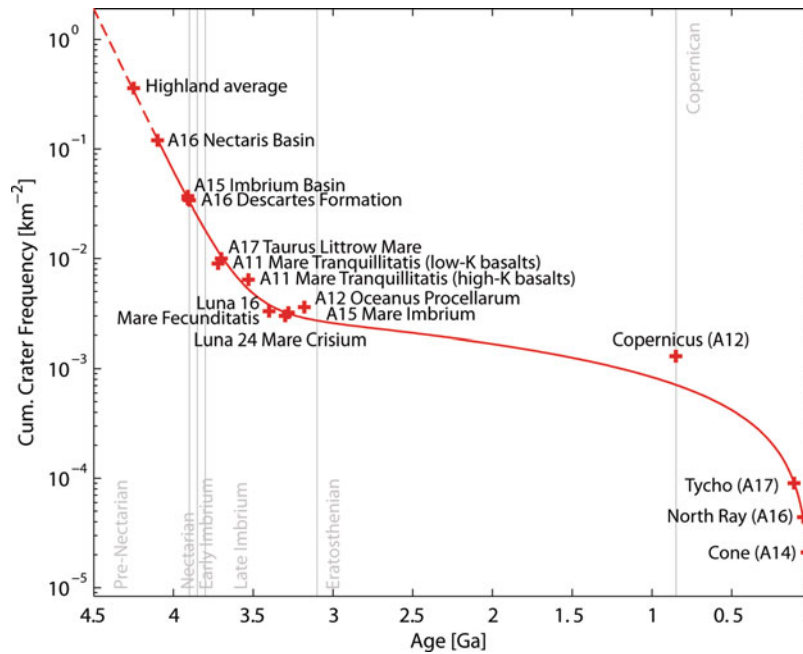


Fig. 4 Cratering chronology model according to Neukum et al. (1975). Calibration points beyond 4.1 Ga (the currently best estimate for the age of the Nectaris Basin, Fernandes et al. 2013) are speculative, and, therefore, earlier cratering rates are debated

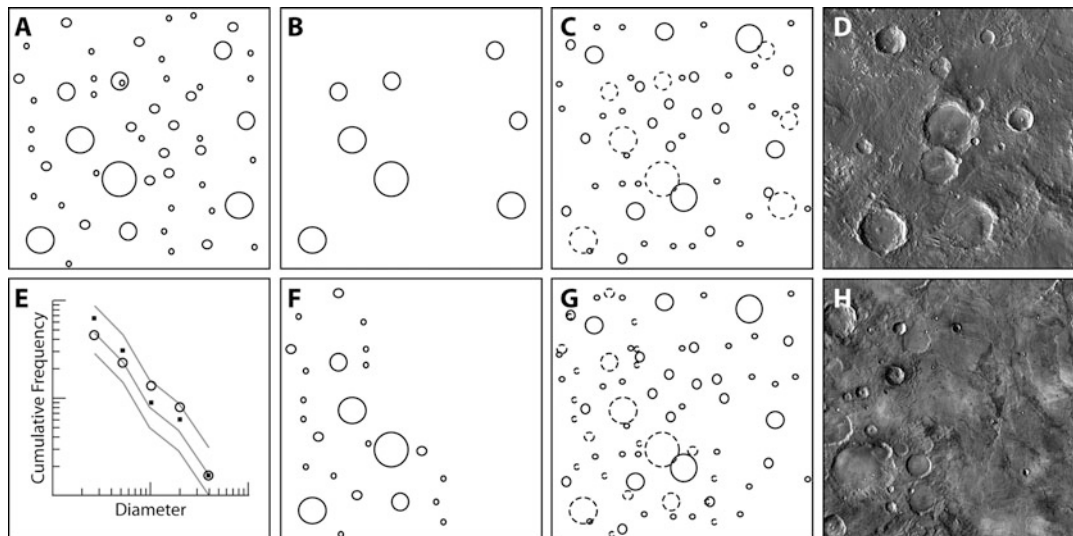


Fig. 5 Cratering. A planetary clock: sequence A, B, and C and sequence A, F, and G depict the effect of resurfacing activity on the crater distribution when (B) the entire unit is partially resurfaced, and only smaller craters were erased, and (F) half of the unit is completely resurfaced. The resulting crater size–frequency distributions are shown in (E) in comparison to artificial isochrons; event (B) as circles, event (F) as squares. Martian surface examples of resurfacing are shown in (D) as caused by erosion and in (H) due to emplacement of volcanic flows

describe the curve relative to a D^{-2} distribution and are used to compare distribution shape variations. The theoretical concept and mathematical background for dating techniques based on crater counts were developed in the 1960s and 1970s, as summarized by the *Crater Analysis Techniques Working Group* (Arvidson et al. 1979).

The sketches in Fig. 5 describe the crater size–frequency distribution modifications as a result of partial and complete resurfacing due to erosion or volcanic emplacement. Both these geological processes can modify the cratering record, and only thorough geological mapping permits a meaningful interpretation of the cratering record. The comparison of measured crater size–frequency distributions and the crater–production function (see below, Fig. 3) can aid the interpretation only if photogeological mapping and crater statistics were performed well beyond the image resolution limit. The relative differences of the calculated areal crater densities are interpreted as relative ages, and geological events at a global scale can be compared even if no superposition relations are detected.

Cratering Statistics and Cratering Rates

The approach of dating planetary surfaces by crater densities (i.e., the number of craters per square kilometer) was first proposed by Öpik (1960), whereas linking crater densities with isotopic ages was pioneered by Shoemaker et al. (1962). The Apollo and Luna sampling missions provided lunar rock samples that were isotopically dated; these isotopic ages were later correlated to crater densities on the lunar surface (e.g., Hartmann 1970). This permitted dating of surface features so that the planetary evolution could be studied through absolute geological time, and thus, the crater counting method is the only tool to date planetary surface evolution when in situ samples are not available.

To determine absolute surface ages of planetary surfaces other than those for the Earth or Moon, some basic assumptions are made: (1) the rate of impact crater formation is known, and the rate is size dependent as assigned by the crater–production function and is stable with time (Fig. 3); (2) the cratering process is spatially and temporally random, i.e., no preferential bombardment seasons exist; (3) target–property variations across the target body are negligible; and (4) surface units are mapped according to geological criteria. The conversion from crater frequencies (relative ages) to absolute ages requires a cratering chronology model. Such models link crater frequency and absolute ages derived from isotope geochemistry and were developed in the early 1970s (the most commonly adopted one is by Neukum et al. 1975, Fig. 4). The crater densities measured on different planetary surfaces that have been exposed for the same duration are assumed to be similar for all planetary bodies.

For planetary bodies beyond the Earth and Moon, the lunar chronology model is transferred to the impact conditions on the other bodies. The scaling of crater sizes between planetary bodies requires knowledge of (1) the flux ratio of impactors at different sizes considering celestial mechanical aspects and (2) how the conditions of crater formation differ from one planet to another. These conditions are mainly defined by mass of the projectiles, impact velocities, impact angles, gravity acceleration, and target properties of the impacted bodies, and are not always fully understood (Werner and Ivanov 2014).

Planetary System Evolution and Cratering Chronology Models

The bombardment history of the Moon is closely related to our understanding of planetary formation and evolution of the solar system. The discovery of extrasolar planets has revolutionized research on the dynamical evolution of our own planetary system. The opportunity to observe planetary systems in evolutionary stages, both younger and older than ours, has inspired ideas of

orbital migration of the gaseous planets during their primordial accretion phases. New dynamical orbital evolution models comprising the orbital inward and outward migration of the gaseous giant planets have emerged, with important implications for orbital changes of the surviving planetesimals (e.g., Tsiganis et al. 2005; Gomes et al. 2005). These models suggest that the average impact velocities have changed through time, making it difficult to relate cratering statistics on old surfaces with crater counts on young surfaces, as increased impact velocities would result in larger crater sizes (Werner and Ivanov 2014). Traditional cratering statistics for planetary surface-age determination assumes monotonic decay of the cratering rate at constant average impact velocities.

Summary

Understanding the evolution of planets in the solar system critically depends on accurate estimates of time and rates at which processes, e.g., volcanism, occur. Absolute time scales for planetary surface evolution in the inner solar system (except the Earth and the Moon) can only be derived by linking the lunar crater frequencies with isotopically dated lunar samples. The crater counting method, the only tool to date in absolute terms planetary surface evolution when samples are not available, is challenged by many observational uncertainties and the great diversity of approaches. Diverse crater–production functions are used to calibrate crater density measurements, which has resulted in a variety of different lunar chronology models. This diversity propagates to other planets such as Mars and adds ambiguity to the related temporal interpretations (e.g., Werner and Tanaka 2011). Commonly used cratering statistics for planetary surface-age determination assume monotonic cratering rate decay, but other interpretations have been put forward due to the discovery of extrasolar planetary systems. Cratering rates prior to formation of the Nectaris Basin on the Moon are not constrained and therefore debated in the light of solar system evolution concepts (Werner and Ivanov 2014). Nevertheless, currently cratering statistics are the only method to determine globally and across the solar system relative and absolute ages and rates of planetary surface evolution, until such time as datable samples will become available from other planetary bodies.

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^{14}C in Plant Macrofossils

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Definition

We discuss ^{14}C dating of plant macrofossils from different contexts and consider the various complicating effects of the history of the samples on the ^{14}C measurement.

Introduction

Late Quaternary chronologies are commonly constructed using AMS ^{14}C dating of plant macrofossils, because they are generally argued to provide the most reliable chronology. Although plant macrofossils are often relatively abundant and well preserved in a variety of site type, they are still potentially subject to a range of complications. Be they terrestrial or aquatic, plant macrofossils are prone to absorb CO_2 of mixed origin during photosynthesis, to be reworked, contaminated by dissolved organic carbon and by modern carbon due to inappropriate storage and analysis. They can also be potentially impacted by measurement effects relating to small sample sizes.

We will overview different macrofossils here, in dry and then humid environments, will give few notes on insects and invertebrates commonly retrieved besides plant macrofossils and finally, we will highlight good practices in the laboratory.

Dry Environments

Numerous archeological and paleoclimatological studies are performed in dry environments and chronological frameworks are then established from (carbonized or non-carbonized) vegetal remains. This section deals with tree products, phytoliths, and pollen.

Tree Products

Every year, tree growth adds wood to the outside part of the trunk. The date measured on heartwood may be already many centuries old by the time a tree was cut down. This is particularly true for long-lived tree specimens, such as oak and juniper. An ideal material to date, if available, would be a twig or branchlet of small trees that can integrate 5 years in the worst case. Seeds and other food remains are also reliable material to be dated. Specific cultural or environmental conditions must equally be seen as potentially impacting radiocarbon dates. This is the case for arid, coastal, volcanic, and “industrial” environments.

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“Old Wood Effect”

The problem of the “old wood” effect in radiocarbon dating has long been recognized for charcoal and wood samples (e.g., timber), the age of which may be hundreds of years older than expected. Besides this, the archeological field faces another difficulty linked to possible time lags between felling and final deposition. The timber may have an extensive history of use and reuse, especially in arid environments where hard trees are rare. We should be aware that the date we are measuring is the death of the tree and not its last use (e.g., Saliège et al. 2012).

Atmospheric CO₂ of Different Origin and ¹⁴C Signature

Costal environnement Significant effect from ocean upwelling can be recorded in some coastal regions. There, ¹⁴C-depleted CO₂ degassing from deep ocean water in an upwelling system can mix with free atmospheric CO₂ and be incorporated by coastal vegetation, which results in older apparent ages, or “ageing.” There are indications that there may be small but significant offsets in Japan (Nakamura et al. 2007). This offset is difficult to assess as it is directly linked to the highly fluctuating ocean circulation and equilibrium.

Volcanic environnement It is also documented that equivalent effects can be local variations close to volcanic vents, where terrestrial macrofossil may be affected by magmatic CO₂ devoid of ¹⁴C (e.g., Cook et al. 2001a; Pasquier-Cardin et al. 1999). Usually, such effects seem to be localized and not be recognized around lakes under windy influence (e.g., Hajdas et al. 1998).

Industrial modern environnement Industrial-scale release of fossil fuel-derived CO₂ can have a similar large local effect, and this could be relevant for the use of radiocarbon dating for historical (postindustrial revolution) times.

Phytoliths

Phytoliths are increasingly used for isotopic studies performed on organic matter embedded into the skeleton-building silicate (e.g., Hodson et al. (2008) and references therein). Phytoliths trap trace amounts of organic carbon (typically 0.1%wt) that is encased in silica (Mulholland and Prior 1993). This very small amount of carbon available for a ¹⁴C measurement requires the highest control of the blank quality (Santos et al. 2010). In a recent study performed in highly controlled conditions, Santos et al. (2010, 2012) showed that phytolith carbon may be released from old soil organic matter and might not be directly linked to the age of the plant, but this is still under debate (Sullivan and Parr 2013).

Pollen

Because many continental paleoclimatic studies are based on pollen assemblages, it appears judicious to directly base the chronology on pollen itself. However, very few ¹⁴C dating attempts were performed on pollen grains themselves (Long et al. 1992; Mensing and Southon 1999), most are performed on pollen concentrate from sediment (e.g., Brown et al. 1989; Kilian et al. 2002; Neulieb et al. 2013; Piotrowska et al. 2004) and the results are highly variable, from a clear rejuvenation, that is, the age is too young, to some hundreds of years older, or an age in agreement with larger identified macrofossil. Hence, pollen dating is still in development.

Humid Environments: Lake, River, and Peat

The main other types of carbon reservoirs, relevant to radiocarbon dating, are lakes, rivers, and peats. Humid environment sediments reflect a variety of different deposits ranging on a scale from purely allochthonous to purely autochthonous, minerogenic, and/or organic material. They may contain, for example, precipitated and/or in-washed mineral matter, terrestrial and aquatic plant and animal remains, including algae, bacteria, and fungi, as well as reworked older organic material. Such freshwater systems not only act as ^{14}C reservoirs in their own right and exchange CO_2 with atmosphere but also incorporate carbonate and organic carbon from surrounding catchments. This means that the radiocarbon concentration can lie anywhere between the levels of the atmosphere and those of the bedrock (zero for geological carbonate).

Generalities on “Freshwater Reservoir Effect” and “Hard Water Effect”

Aquatic cells photosynthesize subaquatically and hence build carbon from dissolved inorganic carbon (DIC) into their cellular material, so they reflect the ^{14}C : ^{12}C ratios of the water from which they grow. The DIC is influenced by (1) exchange with the atmospheric CO_2 reservoir, (2) decomposition of organic matter, (3) residence time of lake or peat bog water and in areas with calcareous bedrock and/or soils, and (4) dissolved carbonate from surrounding limestone catchments. This means that the ^{14}C activity of DIC does not reflect the ^{14}C activity of atmosphere, but it is ^{14}C depleted. This results in an artificial ageing, the so-called freshwater reservoir effect in soft water environments and the “hard water effect” in calcareous areas, inherited by algae cells and which can show wide variation (Fontana 2005; Macdonald et al. 1991).

As example, in arctic oligotrophic lakes, it has been suggested that ^{14}C -depleted particulate and dissolved organic carbon (POC and DOC) transported from soils and peat in the watershed of the lakes may have a large influence on the age of the surface sediments (e.g., Abbott and Stafford 1996) with reservoir ages of up to 1,000 years. In such extreme environments, with lakes of low aquatic production, the allochthonous organic fraction may make up a large part of the total organic matter and may thus influence the composition of the sediments. If the allochthonous fraction consists of old organic matter, washed out from peats and soils, it will obviously increase the age of the sediment. Such considerations may be very important for paleolimnologic studies of lakes with low productivity surrounded by a landscape rich in peat lands and thick soils. Perennial lake ice cover, which seals off the lake water from the atmosphere (e.g., Doran et al. 1999) and/or inflow of glacial melt water (enrichment by old CO_2), may also act in favor of artificial ageing. However, there are some examples of peat bogs that do not seem to be subjected to freshwater effect, such as the case of lacustrine or palustrine environments developed on glacial till (e.g., Blaauw et al. 2004; Hajdas et al. 1998; Walker et al. 2001).

Furthermore, in fluvial systems, the actual radiocarbon concentrations can vary seasonally and depend on details of the recent weather conditions (e.g., Neff et al. 2006). In larger lakes, the variation will generally be slower and reflect long-term climatic trends.

Algae and Aquatic Moss Macrofossils

As “freshwater reservoir effect” and “hard water effect” vary according to environment specificities, their magnitudes affect the relevance of plant macrofossils for dating that are recovered from sediments. Algal macrofossils should thus be avoided if possible. If there is no other choice, an evaluation of the reservoir age should be associated with the measurements. This could be done by the collection, in a “reference” level, of algae macrofossils and subaerial plants. But once again, attention must be brought to the choice of the reference level. Indeed, the level chosen to determine

the reservoir age should correspond to an equivalent climatic context to the one to which the correction will be done.

Relevance/Match of Some Identified Terrestrial Plant Macrofossils

Based on the assumption that superior (terrestrial) plants that photosynthesize from free gaseous CO₂ instead of DIC are less susceptible to contamination by inert carbon than their aquatic counterparts, since they obtain their carbon by subaerial photosynthesis, many scientists have advocated the exclusive use of superior plant macrofossils for radiocarbon-dating lacustrine and palustrine sediment sequences. However, they also are not free of problems.

***Potamogeton* Seeds and Other Floating Superior Plant Macrofossils**

Floating superior plants photosynthesize from the CO₂ available at the water surface that mostly results from a mixture of free atmospheric CO₂ and degassing DIC. Indeed, a high content of mineral carbon in water can result from strong limestone catchment erosion or from high organic matter mineralization, such as is commonly observed following a production bloom that may result in DIC degassing. Consequently, floating superior plants inherit part of the DIC ¹²C:¹⁴C composition, and even if diluted, the “freshwater effect” affects the ¹⁴C activity of *Potamogeton* seeds. The conversion of this activity into a date would induce significant ageing (i.e., the sample appears too old) (e.g., Hatté et al. 2013) or even rejuvenation (too young) in the specific case of modern environments that absorbed high “bomb peak” ¹⁴C. Indeed, the DIC may thus be imprinted by peak bomb organic carbon and then the floating plants appear ¹⁴C enriched (e.g., Olsson and Kaup 2001).

There are some examples of peat bogs where DIC degassing is not significant, and dating obtained on *Potamogeton* seeds gives a reliable chronological framework (e.g., Walker et al. 2001). Nevertheless, since this is linked to water organic production and thus to seasonal cycle, the degassing can fluctuate greatly, and therefore, a quantitative evaluation is difficult. It remains hazardous to work on this kind of macrofossil. Therefore, it is better to avoid the use of floating plant macrofossils for dating as much as possible.

Sphagnum, Terrestrial Mosses, and Smaller-Sized Superior Plant Macrofossils

As ombotrophic peat deposits are very common and sphagnum-formed, sphagnum macrofossils are often used for ¹⁴C dating (Kilian et al. 1995). These superior plants do not grow in the water context and are not subjected to a “hard water effect” or DIC degassing influence; however, they are not free of old carbon effects. Indeed, palustrine areas may be highly organic, especially in ombotrophic bogs, and then very efficient environments for organic matter mineralization. As this mineralization can be from recent as well as old organic matter, the resulting mineralized CO₂ emitted by the “soil” shows an old apparent ¹⁴C age. Thus, at the ground surface, CO₂ results in a mixture between free atmospheric CO₂ and mineralized organic matter CO₂. At a lower scale, this effect can be linked to the well-known canopy effect in a tropical forest. Close to the surface, the smaller-sized superior plants like sphagnum and mosses may thus show ¹⁴C ageing (Jungner et al. 1995). Some mosses are calciphilous and thus may incorporate limestone as a carbon source; this effect may result in an ageing (Zazula et al. 2006). These mosses may not constitute the most reliable support to establish a chronology. Considering the uncertainty ranges associated with ¹⁴C dating, this ageing can sometimes not be significant, and chronologies based on ¹⁴C on sphagnum can be reliable. But with the increasing precision of ¹⁴C dating, the ageing risk linked to organic matter mineralization has to be taken into account.

Tall Superior Plant Macrofossils

Finally, larger superior plant macrofossils seem to be the most suitable macrofossils for ^{14}C dating. A plethora of such macrofossils can be found in peat and lake sediment. We can list needles of *Pinus*, *Larix*, and *Picea*; seeds of *Betula*, *Carex*, and *Eleocharis*; and leaves of *Salix*, *Dryas*, *Erica*, and *Calluna* as the most common.

On account of their high resistance to diagenesis, *Carex* seeds were intensively used in support of chronological frameworks. However, this effective resistance does not permit verification of the state of preservation, and so some possibly reworked or redeposited seeds might not be recognized from indices on macrofossil shape and entirety. This was the origin of some inconsistent chronologies based on macrofossils of several centimeter tall superior plants (Turney et al. 2000). We would recommend the collection of “fragile” macrofossils from which it is easy to check that they are unlikely to have been physically transferred within the sediment matrix and/or otherwise reworked from the surrounding catchment and/or reworked by fauna and/or the rhizosphere. For example, intact *Betula* seeds surrounded by a fragile voile or survival of the fragile *Salix* leaves can be ideal candidates for ^{14}C dating to establish a chronological framework.

Insects, Amphibians, and Invertebrates

Beside plant macrofossils, insects are common and often abundant in a range of sediment types. Examination of their utility as dating materials has focused on bark beetles and chironomids. Beetles sclerites (Elias et al. 1991; Porch and Kershaw 2010) and chironomid head capsules (Fallu et al. 2004; Jones et al. 1993) extracted from lake sediments have shown to provide reliable radiocarbon dates. However, it should be remembered that some animals such as detritus feeding beetles will ingest carbon that might have been photosynthesized some years to hundreds of years before and are part of soil organic matter. They are thus ^{14}C depleted relatively to atmosphere and will result in older than expected ^{14}C ages. In lakes affected by erosion of surrounding catchment, these burying beetle remains can become part of lake sediment and thus also yield for ^{14}C inversion. Finally, aquatic beetle species that feed with algae mimic the addition of old carbon to their food.

Land snails might also exhibit a similar (even more extreme) radiocarbon signature. They can use calcium from limestone as major component of their shells and incorporate at the same time the limestone carbon that, mixed with ingested plant carbon, might result to very high ageing (up to 2,400 years) especially in arid and semiarid regions (Goodfriend et al. 1999). Furthermore, snail shells are quite soluble and chemically interact with the environment. Dissolution and recrystallization are highly probable and would induce apparently rejuvenated radiocarbon age. Humid phases that followed a dry fossilization inevitably imply carbonate dissolution and recrystallization. Dating land snail carbonate should be avoided.

Some animals spend time in different parts of the biosphere. That is the case of amphibians that live in atmosphere and water and of some fishes as salmons and eels that spend part of their life in ocean and then freshwater. They thus get their food from a whole variety of sources. This means that the carbon they incorporate will ultimately come from different primary reservoirs and that animals integrate a large variety of ^{14}C signatures (e.g., Cook et al. 2001b). Disentangling the resulting ^{14}C signal is impossible and this kind of support should be avoided.

Sample Fossilization

Once an organism dies, its constituent parts are constantly being broken and reformed, and usually little remains after a few years. However, in some conditions, most notably waterlogged deposits and very dry conditions, there is better preservation. It is important to remember that this preservation is exceptional and therefore that in most cases, the excavated sample composition is not representative of its original composition.

An important factor to consider is mechanical disturbance and downward movement through bioturbation by roots, burrowing animals and insects, and geological instabilities. The reworking risk can be evaluated by animal and insect identification and by a detailed sedimentological study. A reliable chronological analysis cannot be carried out alone and has to be jointly conducted in a collaborative mind.

The organic materials that survive intact for longest with their original complement of carbon atoms are normally the polymers. The carbon from organisms that degrade is not always lost, but can often present in form of soluble molecules such as dissolved organic carbon or the well-known but poorly characterized humic and fulvic acids. Such components can be recovered from sediment but are highly mobile and cannot however be related to a single organism or to a well-defined photosynthesis event. Even when carbon remains in some stable form (non mobile form), there will usually be many other more mobile carbon-containing compounds and other contaminants that become incorporated into the material remains of an organism. These contaminants will have different origins and so will not share the same radiocarbon signal. Removing these contaminants will be a key step in the lab processing.

In the Lab

Sample Preservation

The core storage and the preparation and identification of small macrofossil samples are usually carried out in a nonsterile environment; however Wohlfarth et al. (1998) have shown that the long-term storage of wet macrofossil samples appears to have a significant effect on radiocarbon age, even when samples are kept cool. Fungal spores and microorganisms can easily be incorporated into the sample. As they might use ambient water carbon as source of carbon besides from fossil leaf materials, they therefore contaminate the sample. Similar findings were previously evidenced for marine cores preserved at 4 °C that were contaminated by recent carbon from modern, terrestrial bacteria (Colman et al. 1996; Geyh et al. 1974). Wet storage of the selected macrofossils should be avoided in order to prevent bacterial/fungal activity and the sample should be either dried at 100–110 °C as quick as possible (Björk and Wohlfarth 2001) or dried under vacuum at lower temperature (60 °C) (Gauthier and Hatté 2008). The choice between these procedures should be done according to the sample sturdiness. Dry samples can then be stored in a clean (850 °C pre-combusted) glass bottle or on clean (400 °C pre-combusted) aluminum foil.

Sample Size

Very small samples are likely to be prone to contaminations, especially lab contamination and allochthonous input. To avoid this high risk, large amount of macrofossils should be sampled if possible. For example, Bronk Ramsey (2008) weighed up a rejuvenation of 840 years consecutively to adjunction of 1%wt of modern contamination in a 20 000-year sample. Such a high

rejuvenation that results in only 1 µg contaminating C in a 100 µg C sample has to be put in regard to the weight of a 1 cm long hair (# 50 µg) and of a pullover fiber (# 15 µg).

Furthermore, a larger than expected scatter in measured values for subsamples lower than 0.3 mg C was reported (Oswald et al. 2005; Stuiver and Pearson 1993). Two factors contribute likely to these findings: the uncertain completeness of the graphitization reaction and the increasing impact on contaminant carbon background (Brown and Southon 1997). An incomplete graphitization reaction yields for ^{14}C fractionation up to -60‰ that could be interpreted in case of decoupled $\delta^{13}\text{C}/^{14}\text{C}$ measurements ($\delta^{13}\text{C}$ measured on gas sample, prior graphitization) as an apparent older age up to 500 years.

The best compromise between the lab risk and the error inherent to macrofossil nature (e.g., linked to freshwater or burrowing effect) should be found. What is the best between an isolated *Betula* seed of few µg and beetles sclerites not perfectly identified in high quantity? That will always remain the question.

Conclusion

It is impossible to suggest a universal strategy for obtaining reliable radiocarbon dates, because each approach has to be adapted to the type of soil, lake, peat bog, and sediment material under investigation, as well as to the objective of the study. However, before deciding on the sampling and dating strategy, the following considerations should be made:

1. What are the scientific objectives of the project in terms of dating?
2. Which type of organic material is available and in which quantity?
3. How will the present and the past environment and climate influence the radiocarbon measurement?

These questions are an important precondition to highlight radiocarbon issues such as freshwater effect and its variability within the study period, recrystallization risk, and multiple ^{14}C reservoirs, etc., and finally to adapt the sampling to the chronological framework one needs to obtain.

Cross-References

- [Lacustrine Environments](#)
- [Peat](#)
- [Radiocarbon Dating](#)

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Skeletal Remains (^{14}C)

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Bone and teeth are complex tissues and thus radiocarbon dating them is also complex. They contain carbon in both organic and inorganic mineral phases. The organic phase is primarily collagen. It is a fibrous extracellular structural protein. The mineral phase is bioapatite. Bioapatite is a biologically synthesized hydroxylapatite that is predominantly calcium phosphate within which carbonate ions are substituted.

Biomineralized tissues tend to survive better than soft tissues after death. Nevertheless, they undergo a variety of structural and chemical changes caused by physical, chemical, and biological agents. Post mortem processes that alter tissue structure and chemistry are termed diagenesis. Diagenetic reactions lead to both the loss of endogenous carbon and the uptake of exogenous carbon. One of the main challenges in radiocarbon dating skeletal materials is reliably removing the exogenous carbon that has accumulated within the sample over time. Many different sample preparation protocols have been developed to cope with different sources and levels of contamination. Each protocol has its strengths and weaknesses and no single protocol is suitable for all sub-fossil skeletal remains.

The origin of bone dating goes right to the earliest publications on the ^{14}C method (Arnold and Libby 1951). The earliest dates were derived from total bone carbon. The reliability of these early measurements was almost immediately questioned because bone dates frequently contradicted dates obtained from stratigraphically associated wood and charcoal. This focused attention on determining whether fractions of bone could be identified that would provide reliable dates, and this objective has propelled bone dating research up until the present day.

Chemical preparation methods have tended to focus either on the organic fraction, principally collagen, or the inorganic mineral fraction, the bioapatite. The following discussion deals first with collagen dating. It begins with a description of the structure of the protein itself, followed by a presentation of the five common methods used for collagen extraction from bones and teeth. The parameters that define collagen purity are presented, and this is followed by a brief consideration of burnt bone dating. Protocols for dating bioapatite, the mineral phase of bone, are then discussed. This entry concludes with a review of a special case of bone mineral phased dating, radiocarbon measurement from cremated or “calcined” bone.

Collagen in Bone and Teeth

Most radiocarbon dates on bone, teeth, tusk, and antler are derived from the radiocarbon content of collagen in the organic phase. This is because, in contrast with bone mineral, collagen does not readily exchange carbon with its surrounding environment.

Collagens are in fact a family of proteins (Nelson and Cox 2009). The major type, Type I collagen, is the primary structural protein in bone. It comprises approximately 20 % of dry bone mass. The

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collagen content of tooth enamel is lower than bone, typically about 3 % by mass. The collagen content of tooth dentin is similar to that of bone.

The genes that encode collagen are highly conserved both between collagen types and across species. Organisms on widely separated branches of the evolutionary tree have collagen genes with similar structure. Consequently, collagen purification protocols can be applied without modification to a wide range of animal species.

A single collagen molecule is composed of three polypeptides hydrogen bonded in a rigid triple-helical rod. A small number of covalent bonds within the triple helix stabilize the structure. Each polypeptide is approximately 350 amino acids in length, with a molecular weight of 100,000 Da. The amino acid composition is unusual in that every third amino acid is glycine, frequently followed by proline and hydroxyproline. Hydroxyproline is rarely encountered in other proteins and so can function as a marker molecule for collagen.

Individual collagen tripeptides are bundled in a staggered array, and these arrays are ordered into higher structures and filaments. Cross-links between molecules accumulate within the filaments over time. Hydroxylapatite crystals form within the arrays and the fibrous nature of these biomineralized structures give bones, teeth, and antlers rigidity and compressive and tensile strength. Collagens are also present in non-mineralized tissues, arranged into both ordered and unordered fibers and sheets. The accumulation of cross-links within and between collagen molecules slowly alters the mechanical properties of collagen-based tissues during life.

Archaeological Collagen

Collagen can survive in archaeological bone for extremely long periods, and survival beyond the 50,000 year radiocarbon time frame is not uncommon. The mechanisms of decay are diverse (Collins et al. 2002). Typically, collagen is progressively lost from archaeological bone during diagenesis. Bones retaining less than 1 % collagen by mass are usually too decayed to be reliably dated. Depending upon the burial environment, hydrolytic reactions can fragment the polypeptides decreasing collagen molecular weight and lowering collagen melting temperature. Condensation reactions that cross-link collagen molecules to other biomolecules can also occur, thereby covalently linking contaminants into the collagen matrix. These changes alter the behavior of the collagen fraction during purification and can reduce collagen yield.

Methods for Extracting Collagen from Bones and Teeth for Radiocarbon Dating

A variety of methods exist for extracting collagen from bones and teeth. Considerations that affect the decision about what method to use include the quantity of bone available, its estimated age, its condition, whether or not other isotopic parameters are to be determined, equipment availability, cost, and other factors. Five methods will be discussed: (1) total collagen purification by the Longin and the Modified Longin method, (2) collagen ultrafiltration, (3) total amino acid purification by ion-exchange chromatography, (4) single amino acid purification including hydroxyproline extraction, and (5) the ninhydrin method.

It is important to keep in mind that although the more elaborate preparation protocols seem to promise more reliable dates, this is not necessarily the case. Theoretically, they more precisely exclude contaminants that infiltrated the skeletal remains during burial, yet the paradox is that more elaborate protocols require more extensive laboratory handling and thus are prone to higher levels of

laboratory-induced contamination. It is very important to carry out the experimental controls so contamination levels are clearly defined.

The Longin Method

Berger et al. (1964) first proposed a collagen isolation method based upon the suspension of bone powder in dilute strong acids such as 0.1 N HCl. Acidification causes the bone mineral to decompose. The mineral carbon is released as carbon dioxide gas; the mineral salts dissolve into the acidic solution, as do soluble organic molecules, and an insoluble collagen-rich organic fraction remains. Contaminants can be washed out of the insoluble fraction without substantially reducing collagen yield. The isolated “collagen” fraction is quite crude, often contaminated with humic or fulvic acids, but radiocarbon measurements of it were a clear improvement over whole bone measurements.

Longin (1971) proposed a simple but powerful modification to this early collagen purification protocol. It utilized the acid extraction of collagen in 0.5 N HCl, but followed this with a gelatinization step that rendered the collagen into soluble gelatin. Heating an aqueous suspension of collagen to temperature of greater than 65 °C causes the triple helices in the individual collagen molecules to unwind, producing randomly coiled, soluble polypeptide monomers. Intramolecular and intermolecular cross-links prevent the polypeptides from completely dissociating. Upon cooling, the solution forms a gel. Triple-helical collagen molecules do not reform, but a high degree of hydrogen bonding links monomers together in a random manner. Depending upon the concentration, the randomly coiled collagen peptides either stay in solution or at higher concentrations form a gel. Gelatin is the common name for this solubilized collagen and denotes both the material and its form.

The rationale of the Longin method is that it is unlikely that contaminants absorbed into the bone during burial would undergo the same change in solubility that occurs with collagen as a result of heating in aqueous solution. The initial acid demineralization step allows the removal of acid-soluble contaminants from the insoluble collagen matrix by simple washing steps, and then gelatinization changes the game so that any remaining insoluble contaminants can be removed from the collagen solution by either centrifugation or filtration.

The Modified Longin method adds a NaOH extraction step after the initial acid demineralization step. If the bone is contaminated with soil-derived organic matter that is insoluble in acidic solution, washes in high pH solutions can extract these from the collagen matrix. As atmospheric carbon dioxide dissolves readily in high pH solutions, the base wash must be followed by another acid wash to ensure that any absorbed atmospheric carbon dioxide is removed before the gelatinization steps.

The Modified Longin method is commonly referred to as an “ABA plus gelatinization” method where ABA = acid/base/acid. It has the advantage that it requires a minimum of equipment and minimal sample handling, but achieves a high degree of purification. The acid–base–acid washing steps can be automated using readily available chromatography equipment, and when carried out in continuous-flow systems, there is an added advantage that extracted contaminants are completely removed from the system during extraction. Finally, the gelatinized collagen can be isolated from near-neutral pH solutions by freeze-drying. This dried collagen solid is easy to handle, store, and archive.

Ultrafiltration

This method is a modification of the Longin method. First suggested by Brown et al. (1988), it exploits the large size of collagen protein (>100 kDa for intact protein monomers) and hypothesizes that contaminants are likely to be much smaller molecules. The method involves isolating collagen by the Longin or Modified Longin method, followed by ultrafiltration using 30 kDa molecular weight cutoff membranes. The retained fraction, containing high molecular weight collagen molecules, is retained and dated, while the pass-through fraction containing low molecular weight contaminants is discarded.

Extensive washing of the ultrafiltration membranes have been found necessary. Higham et al. (2006) suggest using the method in contexts in which bones are several half-lives old, and small amounts of contamination have a large effect on the resulting radiocarbon date.

Collagen Total Amino Acid Dating

Ho, Marcus, and Berger (1969) first proposed a method to date bone by isolating and dating collagen-derived amino acids. Collagen was first isolated from bone by 1.0 N HCl hydrolysis of bone mineral. The proteinaceous residue was then hydrolyzed in 6 N HCl at 100 °C for 24 h. The amino-acid-containing residue was then purified by ion-exchange chromatography. After contaminants were washed through the column, total amino acids were eluted and subsequently combusted for radiocarbon measurement. This approach was also developed by Gillespie et al. (1984). Stafford et al. (1987) published a variant using a mixed-bed ion-exchange resin called XAD-2. The use of ion-exchange chromatography exposed a risk that the ion-exchange columns themselves bleed off carbon that contaminated the sample; care was required to minimize it and control it at the measurement phase.

Hydroxyproline Dating

In parallel with the development of total collagen, amino acid dating was the targeting of specific amino acids. Hydroxyproline, though uncommon in most proteins, is approximately 8–12 % of collagen. Its rarity made it a good marker for collagen and several investigators focused on developing methods for its isolation. Stafford et al. (1982), Gillespie et al. (1984), and others have published hydroxyproline isolation protocols. Until recently, these methods have had relatively little impact on bone dating, probably due to their complexity, concerns about column bleed, and the fact that 90 % of collagen carbon is discarded during hydroxyproline purification.

Recently, new hydroxyproline purification methods have been developed (McCullagh et al. 2010; Marom et al. 2012). The development of preparative scale HPLC systems, new ion-exchange resins with low bleed columns, and improved techniques for the measurement of small radiocarbon samples has made this possible.

The Ninhydrin Method

Ninhydrin is a reagent that reacts with primary and secondary amines. In the presence of a solution of amino acids, ninhydrin condenses with the amino group nitrogen and ultimately releases the carboxyl carbon of the amino acid as carbon dioxide gas. A blue-colored ninhydrin chromophore is also a product of the reaction. Nelson (1991) formulated an elegant two-step protocol for extracting collagen carbon using the ninhydrin reaction, and it has been utilized extensively by Tisnérat-Laborde et al. (2003). In the first step, crude collagen extracts are treated with ninhydrin in a slightly acidic buffered solution. A small amount of carbon dioxide is produced from the terminal amino acid of each collagen polypeptide and any free amino acids or other contaminants in the preparation that contain primary or secondary amines. The first pulse of carbon dioxide gas is discarded. The ninhydrin-treated collagen polypeptides are recovered and then hydrolyzed to their constituent amino acids in hot 6 N HCl. When this preparation is treated a second time with ninhydrin, the resulting carbon dioxide gas is recovered for radiocarbon dating.

Part of the power of the method lies in the selectivity of ninhydrin for collagen amino acids. Burial contaminants comprised of lipids, carbohydrates, humic acids, and other organic compounds are unreactive. Another advantage comes from the phase change that occurs in the carbon of interest during the reaction. The ninhydrin reaction takes place in a solution, but the carbon of interest bubbles out as a gas so unwanted contaminants remain behind.

The main disadvantage of the method is inefficiency. At best, only one tenth of the collagen carbon is available for radiocarbon measurement. There are further complexities if stable isotope data are required, and these were investigated by Keeling et al. (1999).

The inefficiency of the ninhydrin, hydroxyproline purification, and other elaborate protocols that by their nature only recover a small percentage of collagen carbon presents a paradox: Only bones in a good state of preservation contain sufficient collagen so that elaborate purifications are possible, yet if bone preservation is good, then elaborate protocols are probably not needed.

Collagen Quality Indicators

Collagen structure has been elucidated both biochemically and genetically in a broad range of species. A archaeological collagen more difficult to characterize. Nevertheless, several basic parameters are used to define it. Solubility characteristics, carbon content, nitrogen content, carbon to nitrogen ratio, carbon $\delta^{13}\text{C}$ and nitrogen $\delta^{15}\text{N}$ values, glycine content, the presence of hydroxyproline, and other parameters have been used to identify collagen in extracts of archaeological bone. Moreover, these parameters can, to some extent, be used to assess the purity of the preparation (van Klinken 1999). This is in contrast to the short list of parameters that defines the other two most commonly dated organic materials, charcoal and wood cellulose. The identification of contaminants within these materials is much more difficult because the only parameters available are carbon content, which is not particularly enlightening because the principle component of potential contaminants is also likely to be carbon, and $\delta^{13}\text{C}$.

Burnt Bone

Burnt bone and teeth present several challenges for radiocarbon dating. The degree of charring affects the survival of organic material and also changes its chemistry. Consequently, protocols for collagen purification are not reliable and the collagen quality indicators such as carbon and nitrogen content cannot be applied. For these reasons, burnt bone is best avoided.

Carbonate Dating

The crystals of bioapatite, though predominantly calcium phosphate, contain carbonate substitutions to the extent that the mineral phase of bone contains about 5 % of total bone carbon. The carbonate content of bioapatite is about 0.5–1.0 % by weight. The crystal morphology varies within and between bones and teeth and also changes during life, after death, and during burial.

The earliest bone radiocarbon measurements were carried out on total bone carbon and thus included mineral carbon. The variability of such bone dates compared to associated charcoal made it clear that groundwater infiltration during burial could deposit secondary calcite, contaminate the mineral fraction, and thus alter the radiocarbon date. Haynes (1968) demonstrated that acetic acid was capable of removing secondary calcite, and this treatment was adopted within protocols designed to extract stable isotope information from bone and tooth mineral (Koch et al. 1997). In spite of this advance and subsequent attempts to refine it (Haas and Banewicz 1980), radiocarbon dates on mineral carbon persistently generate dates offset from associated charcoal or other organic material. These findings have limited the use of bone mineral in dating studies. Nevertheless Zazzo

and Saliège (2011) have recently called for renewed research on apatite dating because in some environments, typically hot and arid regions, apatite carbon is all that survives.

Calcined Bone Dating

When bone is burnt above approximately 650 °C, as can be encountered during cremation, its mineral structure is altered. The bone fragment, the organic fraction, is completely lost, and the color of the interior becomes pure white. The majority of the carbonate is lost, and apatite crystal size and degree of order (crystallinity) increase (Stiner et al. 1995). The bone becomes “calcined.” Calcined bone is initially very friable after burning but undergoes recrystallization, after which the bones become structurally stable and resistant to environmental carbonate exchange reactions.

Lanting et al. (2001) first demonstrated that the radiocarbon content of calcined bone generally matched the radiocarbon content of associated organic material and concluded that traces of carbonate carbon survived the high-temperature decomposition. Subsequently, calcined bones were shown to give identical radiocarbon dates to stratigraphically related organic material in a variety of burial circumstances (DeMulder et al. 2007; Starkovich et al. 2013). The question of why this is the case motivated considerable research (e.g., Van Strydonck et al. 2005). Subsequently, Van Strydonck et al. (2010) and Hüls et al. (2010) demonstrated that at least some of the carbon within calcined bone originates from the fuel used during cremation. This opened up the possibility that radiocarbon dates on calcined bones might be altered if old wood was utilized during cremation. Evidence of this effect can be seen in Olsen et al. (2008) in which cremated remains were older than associated dendrochronologically dated wood.

Summary and Conclusions

Skeletal remains contain two carbon pools, an organic phase that is primarily collagen protein and an inorganic mineral phase containing calcium carbonate. The organic phase, primarily collagen, is the preferred target for radiocarbon dating because it does not readily incorporate carbon from the burial environment, whereas secondary carbonates from the burial environment readily precipitate within the mineral phase. Diagenesis, the physical and chemical reactions that alter skeletal remains during burial and decay, differs according to the particular chemistry of the burial environment. Thus, the preservation state of a particular bone is difficult to predict. A variety of purification protocols have been developed to isolate collagen protein or subcomponents of it.

Although historically skeletal remains were considered a riskier material for radiocarbon dating than cellulosic materials, their inherent complexity translates into increased information content. Advances in understanding how dateable components in archaeological bone and teeth survive, and how they can be extracted, have made them important materials for radiocarbon dating.

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Big Bang



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The most widely accepted model for how the universe came to be is the Big Bang model. According to this model, the universe expanded from an extremely hot, dense state of essentially zero size (a singularity). From this state, the universe expanded rapidly and cooled. As the temperature dropped, energy was converted to subatomic particles, which then formed protons, neutrons, and electrons. Simple atomic nuclei formed at ~3 min after the Big Bang, but it took ~379,000 years for neutral atoms to form. Over the next billion years, slightly denser regions of the nearly uniformly distributed matter gravitationally attracted nearby matter and began to form clouds, stars, galaxies, and other structures we observe today.

The Big Bang theory is based on three lines of evidence. The first is Edwin Hubble's observation that the farther away a galaxy is, the more redshifted its light is. The spectrum of a light source moving away from us at high speed is shifted to longer wavelengths (toward the red), while that of an object moving toward us will be shifted to shorter wavelengths (toward the blue). Distance can be reliably determined from Type 1a supernovae, which occur in binary star systems where a white dwarf accretes matter from its companion until it reaches the Chandrasekhar limit of 1.4 solar masses. The star is completely disrupted in a thermonuclear runaway that makes a supernova as bright as an entire galaxy. Because the precursor stars of Type 1a supernovae have similar mass, the brightness is always about the same, providing a "standard candle" against which the observed brightness can be calibrated to give distance. The general observation is that galaxies are receding from us in all directions, with those farther away receding more rapidly, much as the points on the surface of a balloon all become farther apart as the balloon is inflated.

The second line of evidence for the Big Bang is the cosmic microwave background that permeates the universe. The microwave background was discovered by accident in 1964 by Arno Penzias and Robert Wilson, who were conducting diagnostic observations at Bell Laboratories using a new microwave receiver. During the initial stages of the Big Bang, all of the particles and photons in the universe were in thermal equilibrium. Atoms and electrons were unbound and photons were continuously scattered by the electrons. Under these conditions, electromagnetic radiation had a black-body spectrum. When the temperature of the universe fell sufficiently, electrons and protons began to combine to form atoms. The scattering of photons ceased and photons could travel unimpeded. As the universe expanded, the spectrum of photons was redshifted. Today, this primordial radiation falls into the microwave region of the electromagnetic spectrum and corresponds to a temperature of ~3 K.

The third line of evidence for the Big Bang is the relative abundances of H and He. The Big Bang model makes specific predictions about how much H and He (and Li, Be, and B) should have been produced as the temperature dropped during expansion. The observed abundances of H and He in the universe match the predictions very well.

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The age of the universe can be estimated from the expansion rate of the universe estimated from the rate at which galaxies are receding from one another and from the temperature of the microwave background. Models of the evolution of the universe from the Big Bang until today have become very sophisticated, giving an age of the universe of about 13.8 billion years.

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Lichenometry

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Definition

Lichenometry dates when a young rock surface was created by measuring the sizes of lichens whose growth rate is known.

Introduction

Lichens are an ancient type of symbiotic growth where algae create food for fungi, that provide shelter for the algae. Their great variety includes delicate foliose lichens growing on trees and rocks. Lichenometry uses only the crustose types (Figs. 1 and 2) that can adhere tightly to rock substrates for a 1,000 years. Figure 2 shows the type of block for dating a block. It has a range of thallus sizes, but only the largest lichen is measured, the assumption being that it most closely approximates the rockfall arrival time.

Recent geomorphic events are dated using the sizes of crustose lichens growing on blocks. Times of landslides, advance and retreat of glaciers, earthquakes, floods, climate change, fires, slush avalanches, and human construction disturbance can all be dated with lichens.

This chapter summarizes the considerable promise of using lichens for accurate, precise dating. First is how to select a field study site and calibrate rates of lichen growth. Then the emphasis is on precision, and diversity, of dating when many measurements allow definition of peaks in a lichen-size distribution.

Lichenometry started in the 1950s (Beschel 1950, 1957, 1959) to study glaciation – at the same time that radiocarbon dating began. But now lichenometry has been virtually abandoned in favor of geochemical methods such as radiocarbon dating of organic matter, optically stimulated luminescence of quartz and feldspar, and cosmogenic radionuclide dating of quartz crystals. The traditional lichenometry method (Innes 1985; Locke et al. 1979) uses only the five largest lichens on moraines left by a retreating glacier. The histogram lichen-size peaks used here are measures of central tendency, not statistical outliers. My New Zealand-California-Sweden database contains ~80,000 lichen-size measurements.

Detailed annual measurements of the entire circumference of lichens by botanists describe highly erratic growth of crustose lichens on rock surfaces (Bradwell 2010; Matthews and Trenbirth 2011). No outward growth may occur for several years, or only one side of a thallus grows. Some presume that dating with lichens is truly hopeless (Loso and Doak 2006). But the circular shape of large crustose lichens is indicative of uniform outward growth over the long term. I avoid erratic growth tendencies by using digital calipers to measure maximum lichen growth. This is the longest axis of the largest lichen on many rock surfaces of interest, such as each 0.5–2 m rockfall block on

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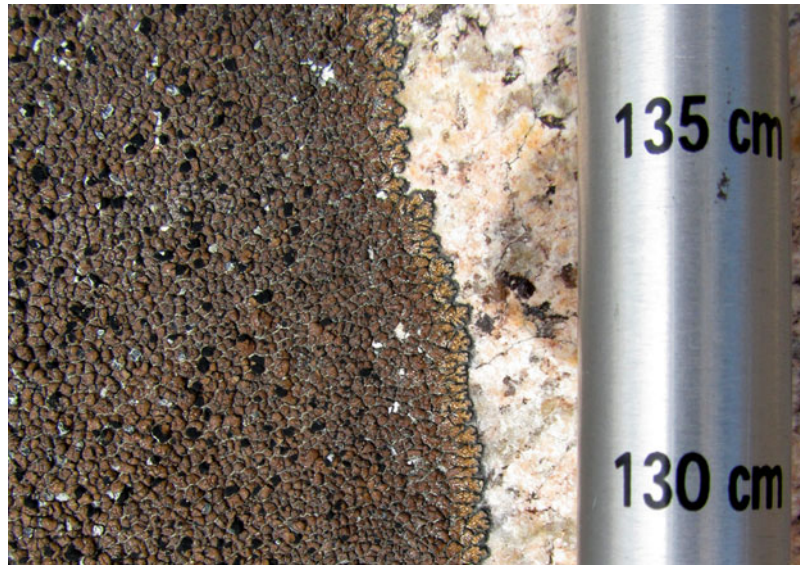


Fig. 1 Edge of large *Lecidea atrobrunnea* in Sierra Nevada of California. Brown and tan are fungal cells; black apothecia reproductive cells contain hidden white spore cases; underlying black algae mat is visible along the right edge

hillside talus or a sequence of adjacent 4 m² areas of beveled rock surface exposed by recent retreat of a glacier.

Calibration of Lichen Growth Rate

Initial calibration of lichen growth rate in California was done in AD 1994 in Yosemite National Park. The long axis of the largest lichen was measured on blocks exposed by construction of a trail to Nevada Falls in AD 1940 and on a AD 1908 landslide that fell off a granitic dome named Liberty Cap. Blocks for an AD 1872 coseismic landslide were identified by cross-dating annual growth rings of adjacent damaged trees. These three calibration points in Fig. 3 span only 68 years, not sufficient for dating old events.

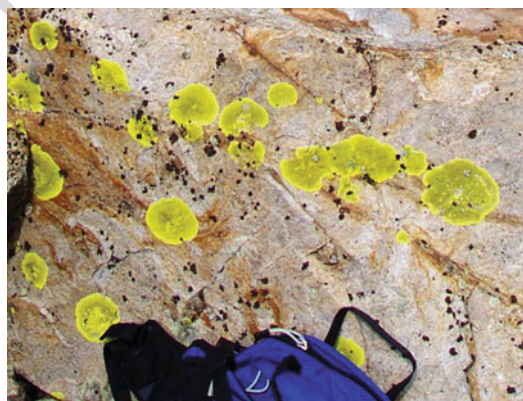


Fig. 2 This 1.8 m long block has many nice *Acarospora chlorophana*. South Fork Kings River, Sierra Nevada, California. The lichen on the right side seems to be the largest; its thallus has acceptable quality for measurement. The handle on the small day pack is 11 cm wide

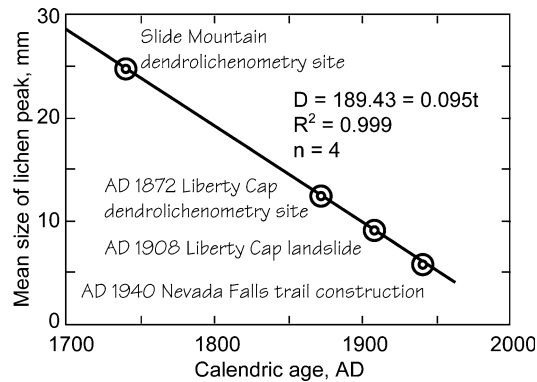


Fig. 3 Calibration of *Rhizocarpon* subgenus *Rhizocarpon* growth rate in Yosemite National Park, California

A prehistoric rock avalanche called “The Slide” (Huber et al. 2002) stopped abruptly in a forest of alpine hemlock trees. Tree-ring analysis dated landslide damage to the forest as occurring between the end of the growing season in September AD 1739 and before the start of renewed growth in June AD 1740. This fourth point in the calibration Figure 3 falls on the same line as the other three points, nicely defining a long-term linear style of lichen growth. Regression of mean lichen size in millimeters, D , and calendric years, t , describes uniform *Rhizocarpon* subgenus *Rhizocarpon* growth as

$$D = 189.43 - 0.095t \quad (1)$$

Uniform-phase growth is a constant 9.5 mm per century. Lichens growing on substrates exposed in the year AD 1 would have a mean size of 189 mm in AD 1994. Calibration of three other lichen species allowed dating of geomorphic processes in diverse climatic settings. Subsequent addition of five new calibration points has not changed Eq. (1).

Site Selection

Site selection determines what lichenometry will date. Markedly different geomorphic processes occur in different parts of the Fig. 4 hillslope. The flume-like features on the left side of the view are debris-flow channels. They have created debris cones with the passage of time. Lichens on debris-flow levee boulders could be used to date individual events and assess frequency of storms capable of creating such events.

Such processes do not occur on the small patches of talus in the lower-right part of the Fig. 4 view. Most of these blocks are detached from their source outcrops by earthquakes. Not much happens between times of seismic shaking, other than freeze-thaw cycles. There are no trees to be uprooted by windstorms, and water flowing off the outcrops just infiltrates into highly porous talus.

The site-evaluation routine for either site is as follows. Hike up the hill to see which calibrated lichens are present: *Acarospora chlorophana*, *Lecanora sierrae*, *Lecidea atrobrunnea*, and *Rhizocarpon* subgenus *Rhizocarpon*. After finding the largest lichen on a block, assess if its thallus quality meets our standards. How smooth and complete are the thallus edges at where we will measure each optimal lichen size to 0.01 mm with digital calipers? Quality ratings of 1 through 4 are assigned to every measurement. Evaluate both transported blocks and the source outcrop joint surfaces from which blocks were derived.



Fig. 4 Diverse granitic mountainside along Lone Pine Creek, Sierra Nevada, California. Debris flows at *left*; rockfall block talus at *right*. Two-lane dirt road in lower left for scale (Image courtesy of Goggle Earth)

We seek a dataset of several hundred measurements; less than 200 is fine if the size range is only 10–50 mm. The Fig. 2 view of *Acarospora chlorophana* is the type of block we prefer. It has a range of thallus sizes; much better than having only one lichen to measure. Very nice, but in this case reconnaissance up the talus slope revealed few blocks with no usable lichens.

Much time is spent finding sites that have many lichens of suitable quality. Surprisingly, some California talus slopes may be completely barren – lichens! Only first-generation crustose lichens growing on fairly smooth rock surfaces should be measured. Rough surfaces, such as coarsely crystalline rocks, provide sizes that are smaller than the same age lichens on ideal substrates such as smooth quartzite joint planes. The finite lifespan of a lichen may be less than the age of the ancient substrate it is growing on. Second- or third-generation lichen growth never dates the exposure time of when blocks were deposited and colonization by lichens was first initiated. These older surfaces typically have a confusing array of small to large lichens that have grown together.

Precise, Accurate Lichenometry Dating

Historical earthquake rockfalls can be used to test the lichenometry method as proposed by Bull and Brandon (1998). The Strawberry Peak site yields typical results (Fig. 5). A first impression may suggest noise instead of actual rockfall events. It looks like too many closely spaced, narrow peaks in the 15–30 mm size range. We need to compare the dates implied by these lichen-size peaks with dates of historical earthquakes (Table 1).

Each peak nicely records the time of a historical earthquakes; so Fig. 5 data noise is minimal. These were large earthquakes – Mw magnitude >6.8. The AD 1857 Fort Tejon event was Mw 7.9 and is recorded by the dominant 29 mm lichen-size peak. It is southern California's largest earthquake. Its epicenter was fairly distant, but ~9 m of right-lateral slip occurred along much of the 350 km long surface rupture that passed only 30 km to the north of Strawberry Peak (http://www.sjvgeology.org/geology/tejon_earthquake.html).

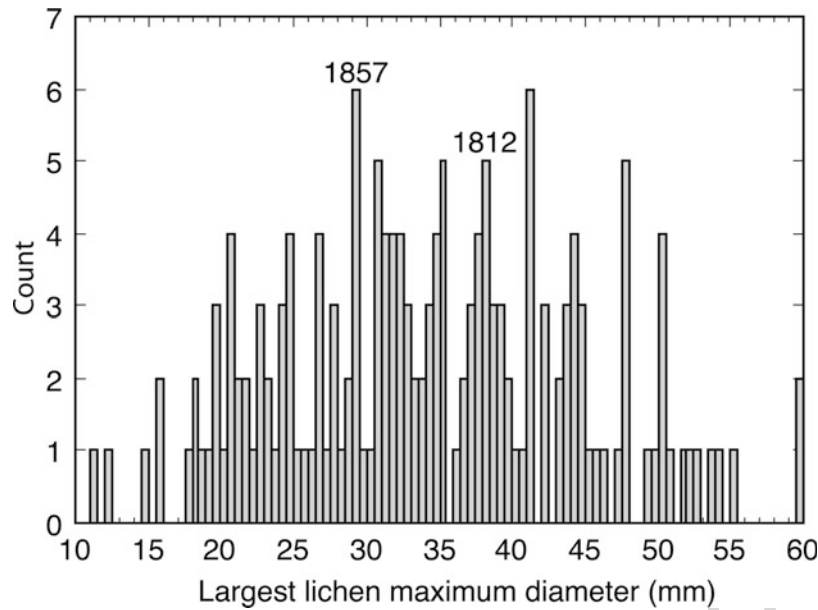


Fig. 5 Distribution of lichen sizes measured in 2013 on rockfall blocks northwest of Strawberry Peak cliffs, central San Gabriel Mountains, Southern California. 0.5 mm class interval. Latitude is 34.28687°N. Longitude is -118.12007°W. Altitude is 1,560 m

The lack of noise in the Fig. 5 distribution of lichen sizes and low earthquake dating error in Table 1 underscore how few nonseismic rockfalls are included in this lichen-size dataset. Careful site selection was essential in order to avoid dating several geomorphic processes.

The broader 37 mm peak records the two big earthquakes of December 1812. The Wrightwood event was on the plate-bounding San Andreas fault to the east, and the Santa Barbara earthquake to the west occurred offshore. Both had strong foreshocks and aftershocks.

The AD 1882 date for the 24.75 mm lichen-size peak does not match the time of a known earthquake. This peak occurs at many sites; being regional implies a seismic-shaking origin. Historic earthquake records can be incomplete in both New Zealand and California (Bull 2007).

Table 1 Accuracy of dating historical California earthquakes using the lichen-size peaks of Fig. 5

Earthquake name (s)	Date, AD	Distance to epicenter	Lichen-size peak, mm	Peak Date AD	Dating error, years
Wrightwood, Santa Barbara	1812.9	40 160	37.75	1813.3	0.4
Fort Tejon	1857.0	170	29.25	1858.2	1.2
Hayward, San Francisco	1866.8	540	27.75	1866.1	0.7
Lone Pine	1872.9	250	26.75	1871.9	1.0
			24.75	1882.0	
Laguna Salada	1891.3	370	23.00	1892.1	0.8
San Jacinto	1900.0	170	21.00	1901.9	1.9
San Francisco	1906.3	550	19.75	1908.5	2.2
Imperial Valley	1915.5	270	18.25	1916.4	0.9
Long Beach	1933.2	60	15.75	1929.7	3.5

Dating Method	~1715 AD event	~1615 AD event	~1580 AD event
Lichenometry	1716 AD ± 2.80 n=10	1613 AD ± 1.78 n=9	1579 AD ± 2.08 n=8
Tree-ring analyses	1716 AD ± 2.78 n=12	1615 AD ± 2.58 n=9	1578 AD ± 3.12 n=9

Fig. 6 Comparison of dendrochronology and lichenometry dating of prehistoric earthquakes on the Alpine fault, New Zealand. From Bull 2007, p. 234. n is the number dates for an event

Even a Mw magnitude 7.5 San Andreas fault event was missed until recognized recently by Toppozada and Borchardt (1998).

Four event epicenters (Table 1) were at least 250 km away. Recording the strong San Francisco earthquake of 1906 is not surprising. That event was felt even farther away, 150 km to the east according to Ellsworth (1990).

A mean lichenometry dating error of about 2 years is the same accuracy as for other studies in New Zealand, California, and Sweden (Bull et al. 1995; Bull 1996a, b, 2003). Bull-Brandon lichenometry dating has a conservative ± 5 -year estimate of dating precision. Such consistent quality can only be cross-checked by still better dating methods – dendrochronology and historical records. Calibration site ages should be known to the year.

New Zealand tree-ring analyses and lichenometry precisely dated three prehistorical earthquakes. Trees were killed, and marked suppressions of annual growth rings occur in New Zealand cedar (*Libocedrus bidwillii*) at the seismically sensitive sites. One is a boggy swamp and the other is a cliffy ridgecrest directly above the 45° dipping plate-bounding Alpine fault. The times of these forest disturbance events were synchronous (± 2 years at the 95 % confidence level) with times of regional rockfall events dated by lichenometry using *Rhizocarpon* subgenus *Rhizocarpon* (Fig. 6).

Lichen-Kill Events

Univariate scattergrams detect lichen-kill events caused by climate change or fire. A scattergram shows the sequence of lichen-size measurements made while slowly traversing across a bouldery deposit. Uniformly dispersed talus accumulating during frequent events has a scattergram with constant density of measurements and range of lichen sizes across the entire traverse. There is a systematic decrease in density abundance for the largest lichen sizes. This decrease is attributed to the removal of old lichens by death or burial by incoming younger blocks. In contrast, a snowkill or firekill event is revealed by a scattergram that has an abrupt decrease in density with increasing lichen size. A transition to markedly lower density marks the approximate time of the lichen-kill event.

Dating a Fire Event

A New Zealand talus site called Cattle Gully highlights a firekill event. The scattergram (Fig. 7) shows two density domains; the transition at 47 mm dates to about AD 1700. Dating precision is lower for scattergrams than for the Fig. 5 histogram. Pieces of charred, rot-resistant *totara* wood on

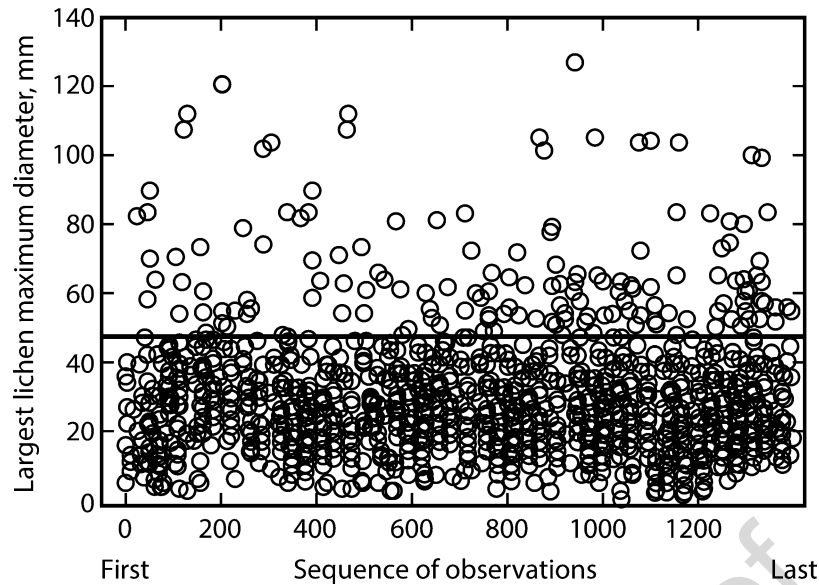


Fig. 7 Univariate scattergram of *Rhizocarpon* subgenus *Rhizocarpon* size measurements at the Cattle Gully site, South Island of New Zealand, reveals two lichen-size measurement domains. Measurement densities are different above and below the 47 mm line; the time of a firekill event that killed most lichens; $n = 1,388$. Bull and Brandon 1998, Fig 12C

the Cattle Gully hillslopes suggest that fire may have killed many lichens, perhaps as newly arrived Maoris used fires for clearing travel routes and flushing game (McGlone 1979).

Dating Climate Change

Times of colder climate in the high Sierra Nevada of California occurred during a recent cooler global climate known as the Little Ice Age. Valley glaciers became larger and many snowfields became permanent, killing lichens after ~3 years of burial. Lichens would recolonize these surfaces as snowbanks melted.

A lichenometry transect across the Chickenfoot glacial moraine of latest Pleistocene age records two of the Sierra Nevada snowkill events of the past 1,000 years (Fig. 8). These data show largest lichen maximum diameters on consecutive blocks. A 200 mm *Lecidea atrobrunnea* would date back to about AD 1070, well before the onset of the Little Ice Age.

The density distribution of the first 200 lichen-size measurements is similar to a height of 150 mm. Few lichens were found above this size. Establishment of a perennial snowbank would kill all lichens except those on blocks that rose above the snow. It appears that the Little Ice Age began here shortly before 150 mm time. A pulse of persistent snow cover ended and recolonization began at about AD 1290. The even distribution of lichen sizes below the 150 mm horizontal line indicates that this part of the measurement transect was not subject to further snowkills.

An article by Miller et al. 2012 about causes of the Little Ice Age postulates that cooling was caused by episodes of SO₂-rich volcanic eruptions that also affected oceanic circulation. When did it begin? End? “summer cold and ice growth began abruptly between AD 1275 and AD 1300.” The Miller et al. data suggest that the Little Ice Age ended by AD 1850.

The next 220 lichen-size measurements along the Fig. 8 transect are much smaller; none are larger than 76 mm and most are smaller than 20 mm. A second snowkill event ended at 20 mm time

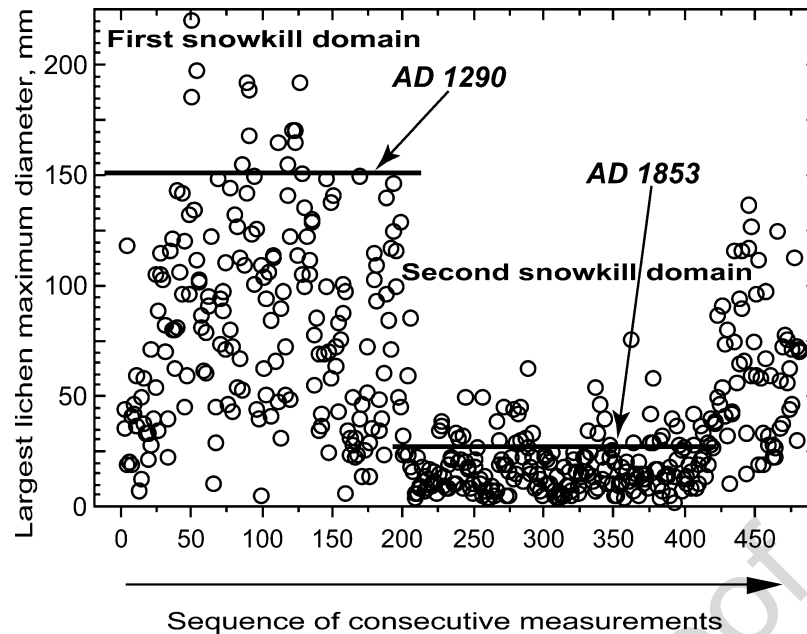


Fig. 8 Univariate scattergram of *Lecidea atrobrunnea* at the Chickenfoot moraine lichenometry site, altitude of 3,540 m, in the Sierra Nevada of California. Two domains of anomalous decrease in density of lichen sizes that suggest times when snowkill events ended. $n = 481$. Bull and Brandon 1998, Fig 12B

(AD 1853 $\pm$ 10 years). The many lichen sizes between 5 and 20 mm suggest that renewed additional colonization did not occur on all blocks at the same time. The thickest, more persistent snow took longer to melt. Other Sierra Nevada sites with different topographic settings might reveal times of multiyear snowfields between AD 1290 and AD 1850.

Discussion

The crustose lichens used in these studies seem to have a preferred geographic distribution and abundance. Most are found in cooler latitudes, or above 1,000 m altitude in mid-latitude and low latitude mountains. This may restrict areas where lichenometry can be used. Fortunately, rocky mountain ranges are common. Detailed information about how landscapes evolve is a major virtue of lichenometry, but only for the past 1,000 years for most studies. Precise surface-exposure dating of fluvial, glacial, and mass-movement landforms can be used to address landscape change rates and the frequency of geomorphic hazards to humans. Landslides, floods, and seismic shaking can be deadly.

Reconnaissance and measurement field time are the main costs. Fieldwork is a mix of working at sites of known age to calibrate and further test rates of lichen growth for several species of a genus, and collecting longest-axis lichen size data at other sites to better understand the history and extent of a geomorphic process. After calibration of a lichen growth rate is complete, the cost per lichenometry age determination is quite low, and one does not have to wait months or years for expensive laboratory work to be completed. The more expensive aspect of lichenometry is the field time spent in finding good sites and collecting representative samples of lichen sizes.

Botanists wonder why geologists assume that crustose lichens grow in a predictable manner that can be defined with an equation, when their year-to-year measurements suggest nonsensical confusion. Geologists would like botanists to tell them why each crustose lichen does not vary in

growth rate throughout the varied climate of a lofty 600 km long mountain range such as the Southern Alps or the Sierra Nevada.

The lichenometry method of dating summarized here is precise and accurate. Lichenometry is a surface-exposure type of age determination, so it dates the actual time of an event. The vastly more popular radiocarbon dating method estimates the time of formation of organic matter created before or after the event of interest, such as rupture of layered sedimentary deposits.

Suggested Innovative Studies

Human-induced global warming has reached the point where record high temperatures greatly outnumber record lows and storms seem ever more powerful and prolonged. Lichenometry can be used to assess recent retreat of glacial ice that leaves behind moraines of lichen-covered rocks. How much deglaciation is the result of natural climate variation? Does acceleration of montane glacier retreat in places such as the Andes, Himalayas, and Europe match the trend of an ever-increasing carbon dioxide in the Earth's atmosphere? What is the pace of retreat of the Greenland ice cap? Have any recent lichen snowkill events occurred, indicative of climate variability? Arctic lakes have diminished and some are now gone (Smol and Douglas 2007). We should date ages and rates of retreat of now-exposed rocky shorelines, comparing small ponds with large lakes. The timespan for these studies should start before the industrial revolution at ~ AD 1750–1800.

Southern California earthquake studies have focused on radiocarbon dating of surface ruptures by the plate-bounding San Andreas fault (Biasi and Weldon 2009). We know little about other prehistoric earthquakes that occurred between the San Andreas fault events of AD 1812 and AD 1680. How frequently did strong regional seismic shaking occur in Southern California during recent prehistoric times? Seismic shaking decreases with distance away from an earthquake epicenter. So, mapping the decrease in coseismic rockfall abundance should be a useful proxy for seismic shaking. Lichenometry suggests that 13 strong regional seismic-shaking events occurred between AD 1680 and AD 1812. Four are recorded by the 41, 44, 48, and 50 mm lichen-size peaks of Fig. 5 of this article. How did the intensity of seismic shaking for these recent prehistoric events compare with the San Andreas fault events of 1680, 1812, and 1857? Lichen-size data from sites in three mountain ranges could be used to make maps depicting regional seismic shaking to compare with maps for seismic shaking caused by the 1812 and 1857 earthquakes.

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Meteoritic ^{10}Be

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Synonyms

Atmospheric ^{10}Be ; Fallout ^{10}Be ; Garden-variety ^{10}Be

Definition

Most terrestrial beryllium-10 (^{10}Be) is produced by spallation of nitrogen and oxygen nuclei in the atmosphere by cosmic rays. The relatively high atmospheric production rate of ^{10}Be (global mean of $\sim 10^6$ atoms $\text{cm}^{-2} \text{year}^{-1}$) varies regionally by latitude by a factor of ~ 2 (Lal and Peters 1967). Meteoric ^{10}Be is scavenged quickly from the atmosphere by aerosols and is transported to the Earth's surface, mostly by precipitation. When ^{10}Be falls onto land, it binds tightly to soil particles. Stable soil with prolonged exposure to rain becomes highly enriched in ^{10}Be , whereas soil in areas of high erosion accumulates little ^{10}Be . When ^{10}Be falls on water, it eventually accumulates on sediments or in precipitates. Movement and cycling of ^{10}Be in the Earth's reservoirs has been reviewed in detail by Morris et al. (2002) and Willenbring and von Blanckenburg (2010).

In recent years, ^{10}Be has been measured most widely in continental ice cores to determine snow accumulation rates and for comparison with cosmogenically produced radiocarbon to determine variations in solar activity through time. Meteoric ^{10}Be is used for a growing number of geomorphic studies including discriminating river sediment sources, understanding soil transport, and quantifying long-term sediment fluxes from watersheds. Beryllium-10 is radioactive with a half-life of 1.39 million years and is often used in conjunction with the native, stable nuclide beryllium-9 (^9Be) to account for variable absorption behavior. The $^{10}\text{Be}/^9\text{Be}$ ratio is used in deep-sea sediments for estimating ages via ^{10}Be decay, for calculating the growth rates of manganese encrustations, and for understanding the past variability in the Earth's magnetic field and chemical weathering fluxes.

Most natural concentrations of ^{10}Be range from $\sim 10^3$ atoms g^{-1} in rain and ice to $\sim 10^6$ – 10^8 atoms g^{-1} in marine and terrestrial sediments. These levels are now easily measured by accelerator mass spectrometry after a chemical process to purify the Be from other elements and boron – an isobar and the daughter product of ^{10}Be decay (Granger et al. 2013). Well-known geochronologic techniques using cosmogenic ^{10}Be called surface exposure dating typically uses the abundance of ^{10}Be produced in situ within crystal lattices of minerals rather than the abundance of meteoric ^{10}Be . The larger flux of meteoric ^{10}Be (on a per-surface-area basis) that is about two to four orders of magnitude greater than the rate of in situ production complicates the chemical purification of the in situ produced component by contamination of grain surfaces. Etching is specifically carried out to remove every trace of atmospheric ^{10}Be adhered to surfaces of grains.

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Mass Spectrometry

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Definition

Any of a number of methods used to determine the spectrum of isotopic abundances in a given material based on the measurement of relative masses of atoms or molecules present in that material. As applied to scientific dating, mass spectrometry is most commonly used to determine abundances of parent and progeny isotopes in naturally radioactive decay systems that have half-lives of geological relevance (years to billions of years).

Introduction

Scientific methods for dating materials of geological interest commonly utilize natural radioactive isotopes that spontaneously transform to progeny isotopes at constant and well-known rates of decay. In order to use this property to estimate absolute ages, it is essential to accurately determine the abundances of both parent and progeny isotopes in a mineral or rock sample that has remained closed to isotopic exchange with its surroundings since its formation. Decay counting can be used to quantify abundances of short-lived radioactive isotopes. However, for radioactive isotopes with half-lives longer than a few thousand to tens of thousands of years, only a small number of atoms undergo radioactive decay during the counting period resulting in poor precision of isotope abundances. Furthermore, a number of geochronometers rely on stable, albeit radiogenic, progeny which cannot be measured by decay counting. Therefore, isotope ratios are more commonly determined by mass spectrometry where potentially all of the atoms present in the sample can be counted. Geochronological methods using K-Ar, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os, U-Pb, and U-Th decay schemes take advantage of atom counting by mass spectrometry to provide precise measurements of relative isotope abundance. Other methods for measuring mass ratios exist; however, this entry focuses on mass spectrometric methods that are most commonly employed in geochronological studies.

Determination of isotope ratios by mass spectrometry involves (1) introduction of the sample into the mass spectrometer either as a gas, liquid, or solid and ionization of the element or elements of interest, (2) separation of ions on the basis of their mass-to-charge ratios, and (3) detection of those ions by measuring currents for large signals or by ion counting for smaller ones. Methods by which material is introduced and ionized allow mass spectrometers to be classified into different types, each of which has strengths and weaknesses. However, all methods take advantage of the physical response of moving charged particles through a strong electromagnetic field and conversion of the beam of separated ions into an electronic signal that is directly proportional to the number of atoms

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detected. Output takes the form of a mass spectrum of peak intensities that are indicative of the relative abundances of isotopes present in the sample, which can then be interpreted to represent age information through application of various decay schemes and dating models. More detailed explanations of the general principles and various methods of mass spectrometry are readily available (Faure 1986; Dickin 2005; Goldstein and Stirling 2003; Faure and Mensing 2005; Gross 2011; Ireland 2013; White 2013).

History

The initial development of mass spectrometry closely followed the discovery of radioactivity in the middle to late 1890s. The first demonstration that isotopes could be separated on the basis of their masses came in 1913 when J.J. Thomson constructed a spectrometer at the University of Cambridge Cavendish Laboratory that used a photographic emulsion to show that neon gas produced two spectral lines of differing intensities representing ^{20}Ne (90.48 %) and ^{22}Ne (9.25 %). Modifications of the original design made shortly thereafter by A.J. Dempster at the University of Chicago in 1918 and F.W. Aston at the Cavendish Laboratory in 1919 included addition of 180° sector magnetic fields enabling directional refocusing, separate thermal ionization filaments to produce and accelerate ions, source and exit slits to better refine the ion beam, and a separate electric field to remove the velocity spread and yield point images (Fig. 1a). Even though early instruments had low-mass resolution and sensitivity, they were capable of identifying all of the naturally occurring isotopes of the light elements as well as their relative abundances.

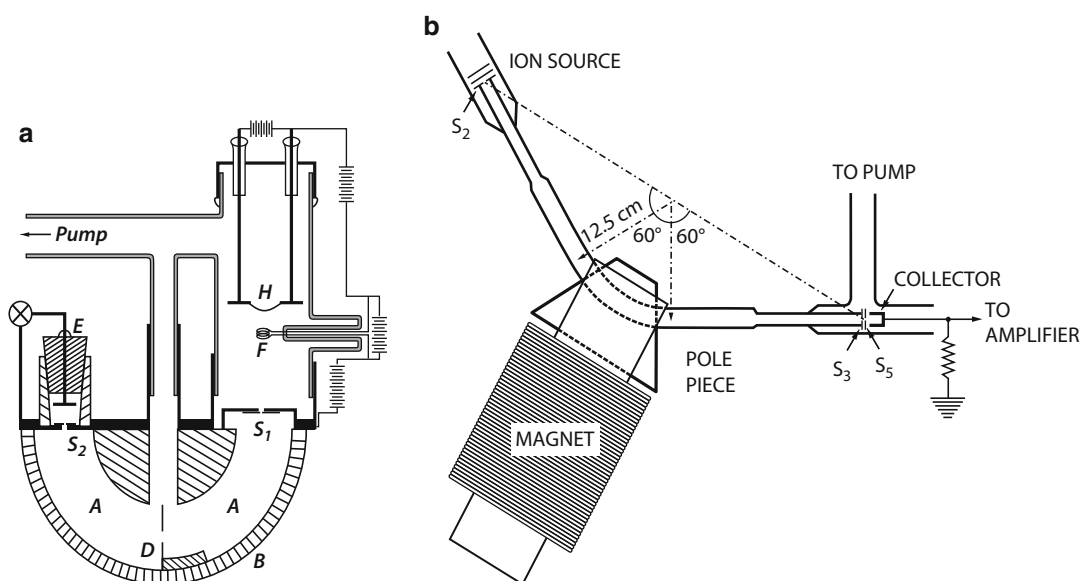


Fig. 1 Historical mass spectrometer designs. **(a)** Cross-sectional schematic of Dempster's first thermal ionization instrument which included an analyzer chamber *A*, constructed from a brass tube fitted with iron plates *B*, an entrance slit *S1*, exit slit *S2*, and defining aperture *D*. The source consisted of an electron-emitting filament *F* and a heating element *H*. Ion currents were detected by the electrometer fitted in an ebonite plug, *E* (Figure modified after Dempster 1918). **(b)** Cross-sectional schematic of Nier's 1940 thermal ionization mass spectrometer consisting of widely separated source and collector whose slits *S2* and *S3*, respectively, are collinear with the center of curvature of the flight tube (Modified after Fig. 2 of Nier 1940). The flight tube passed through a 60° magnetic sector analyzer and had a length of 58 cm between *S2* and *S3*. The basic design has remained similar after more than 70 years of improvements

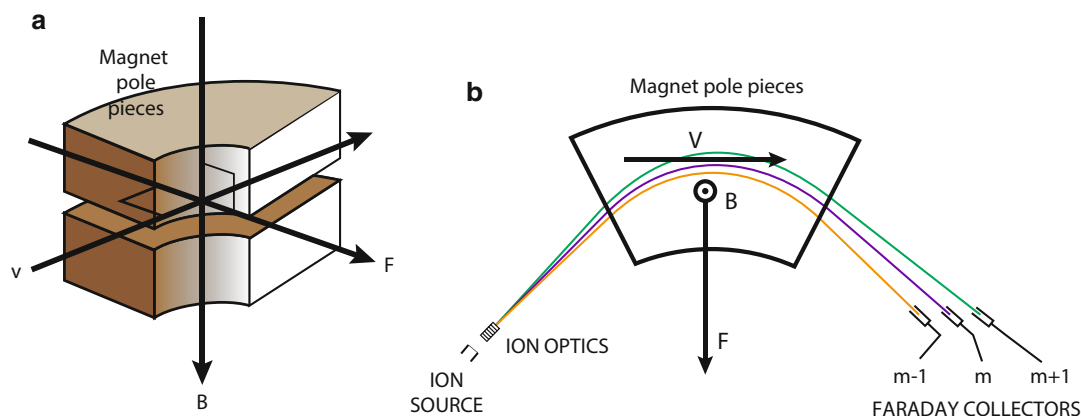


Fig. 2 Diagram depicting the Lorentz force law operating in magnetic sector mass analyzers. **(a)** Oblique schematic view of the magnetic pole pieces designed to provide a uniform magnetic field B . The resulting force (F) operates at right angles to both the ion velocity vector (v) and the magnetic field vector (B) at any point along the flight path. **(b)** Plan view showing the paths of ions of different masses (m) affected by the Lorentz force to different degrees. Ions with heavier masses ($m + 1$) follow less curved paths than ions with lighter masses ($m - 1$)

In 1940, Alfred Nier at the University of Minnesota revolutionized mass spectrometry by developing a design that utilized a 60° sector-field magnet and moved the ion source and ion collectors away from the influence of the electromagnet (Fig. 1b; Nier 1940; De Laeter and Kurz 2006). Nier also completely redesigned the ion source and introduced the electronic measurement of ion beams. These fundamental changes made production and operation of magnetic sector mass spectrometers more efficient and reliable and opened the field of isotope geosciences far beyond the initial scope imagined by earlier physicists. Many modern instruments still use Nier's designs.

Subsequent improvements in mass spectrometer performance are more related to incorporation of digital operation and control, refinement of various electronic and vacuum technologies, and innovation in sample introduction into the ion source. Improvements in instrumentation coupled with the use of clean-laboratory conditions to minimize contamination were stimulated by the lunar sample return missions in the late 1960s and early 1970s and the accompanying interest in understanding solar system evolution by studying meteorites with low elemental abundances for many of the geochronological systems. The development of the plasma source coupled to a multicollector magnetic sector system represented another major wave of improvements in the mid-1990s, allowing the measurement of isotopic ratios for nearly any element in the periodic table.

Principles of Mass Spectrometry

Mass spectrometers are designed to separate ions based on their mass-to-charge ratio. To do this, atoms or molecules of interest in a sample must become charged forming an ion cloud, extracted from that cloud by applying an acceleration voltage (typically 1–10 kV), and focused into a narrow beam using a series of source plates that constitute the ion optics of the instrument. Ions in the accelerated beam have kinetic energy that is equal to the electrostatic field produced in the source ($\frac{1}{2}mv^2 = qV_E/d$; where m = mass, v = velocity, q = charge, V_E = extraction voltage; and d = distance over which the acceleration takes place). The beam thus produced is introduced into a mass analyzer where dispersion takes place using magnetic fields (magnetic sector instruments), rapidly cycling electric fields (quadrupole instruments), or velocity selection (time-of-flight instruments).

Magnetic Sector Instruments

An ion with mass and charge traveling at velocity through a uniform magnetic field (B) will experience a centripetal force that imparts a circular motion. As a result the ion will follow a curved path having a radius (R) within a plane perpendicular to the magnetic field ($F = qvB = mv^2/R$). Magnetic sector mass spectrometers take advantage of this principle (Lorentz law) by using electromagnets specifically designed to produce a homogeneous field that is positioned at right angles to the path of the ion beam (Fig. 2). Ions traveling through the magnetic field will follow an arc with a radius proportional to its mass ($R = mv/qB$). As other factors are held constant, ions of different masses follow paths with different radii through the magnetic field, with heavier ions being deflected less than lighter ones.

To steer beams of lighter and heavier ions into the collector slit on a single-collector spectrometer, either the magnetic field or the velocity of the ions (via changes to V_E) can be varied to alter the radius of curvature via the Lorentz law. In practice, the magnetic field is more precisely monitored using a Hall probe that senses the field strength and adjusts the magnet power supply as necessary (Dickin 2005). In multicollector instruments, a number of faraday cups and ion counters are positioned to simultaneously measure multiple dispersed beams, thus avoiding temporal variability in the signal due to ion beam instabilities. Recent advances in magnet design feature poles set at oblique angles to the exiting beam in order to use fringing fields for better focusing. Because this design also increases the distance from the magnet to the ion focal point, it is referred to as “extended geometry.” This design allows increased ion transmission and greater dispersion, which, in turn, facilitates additional collectors. Ion transmission in magnetic sector instruments can be close to 100 %, whereas multiple-sector instruments commonly have lower transmission.

High-precision measurement of isotope ratios needed for geochronology requires that magnetic sector mass spectrometers maintain very high vacuum throughout the ion path in order to avoid reduced velocities or loss caused by inelastic collisions with ambient air molecules. Pressures within the flight tube (ion path between the source and collector) typically are between 10^{-9} and 10^{-8} mbar. High vacuum is maintained by continuous pumping using a combination of turbo pumps (momentum transfer pump that uses high-speed rotating blades to capture gas molecules) backed by positive displacement mechanical pumps, cryotrap (cold fingers), and ion getters (entrapment pump that uses electrical fields to ionize gas molecules that are then captured on a charged solid substrate).

Quadrupole Instruments

Although magnetic sector mass spectrometry is the most common method used for measurements of high-precision isotope ratios, dispersion of isotopes on the basis of mass-to-charge ratios also can be accomplished by applying electric fields to two pairs of metal electrodes forming a quadrupole mass analyzer (Miller and Denton 1986). Opposing pairs of rods are electrically connected, and a combination of fixed DC and alternating RF (radio frequency) potentials are applied such that two rods have oscillating positive and negative voltages. Ions are extracted from an inductively coupled Ar plasma source and introduced at one end of the quadrupole. Oscillations of charges on the electrodes cause complex ion trajectories where only ions with the proper mass-to-charge ratio for a given set of voltages can traverse the length of the quadrupole. All other ions will have unstable trajectories and be neutralized by collisions with the electrodes. Ions that enter the collector slit at the far end of the quadrupole are measured as described above.

Quadrupole mass spectrometers benefit from the ability to switch masses very quickly allowing collection of data from the entire periodic table during a single, rapid analysis. They require only modest vacuum conditions and are not as complex or costly as magnetic sector instruments. These

attributes allow quadrupole instruments to excel in determination of elemental concentrations in either solution mode or attached to a laser ablation system. However, quadrupole instruments are not as sensitive nor as stable as magnetic sector instruments and are typically operated at unit mass resolution, which typically restricts their use to low-resolution applications (Gross 2011). Therefore, they cannot produce the same level of high-precision, isotope-ratio data compared to magnetic sector instruments and are not widely used in geochronological studies.

Time-of-Flight Instruments

Time-of-flight (TOF) mass analysis relies on the fact that heavier ions are accelerated more slowly than lighter ions of the same charge in the same potential field. TOF instruments are designed to measure differences in arrival times of ions that are generated during a discrete event. In practice, a group of ions is typically generated using a pulsed laser shot, a pulsed beam of primary ions, or a pulse generator coupled with a plasma source. Mass separation is accomplished in the flight tube as ions in the pulse are separated into individual packets defined by mass number. Additional mass dispersion can be accomplished by extending the path length through incorporation of reflection geometries.

Time-of-flight analysis has been primarily used to produce elemental and molecular maps of solid surfaces as well as depth profiles in material-science applications. Benefits include a theoretically unrestricted mass limit, analysis of a complete mass range for a single ionization pulse, high ion transmission, and extremely small sample requirements ($<10^{-18}$ mol). However, time-of-flight analyses generally do not produce fully quantitative data and, as such, have not yet been used to produce geochronological information.

Double-Focusing Instruments

Production of ions in mass spectrometers using plasma sources or secondary ion sources results in ions with a range of kinetic energies as well as mass-to-charge ratios. Dispersal of ion energy results in poor mass resolution due to beam spread and increased tailing. In order to narrow the spread of ion energies and improve mass resolution, both an electrostatic analyzer (ESA) and a magnetic sector analyzer are used in series, resulting in a double-focusing mass spectrometer (Fig. 3). The ESA consists of a set of two concentric curved plates held at different potentials to filter and focus the ions traveling through them, regardless of their mass. The ESA may be placed before (forward geometry) or after (reverse geometry) the magnetic sector. The use of double-focusing designs is critical for

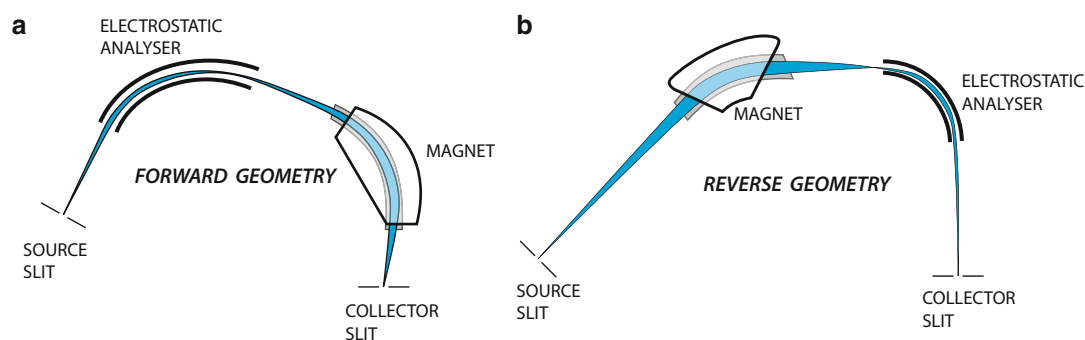


Fig. 3 Schematic depictions showing the ion beam paths (in blue) passing through two types of double-focusing mass spectrometers. Designs employ both magnetic sector analyzers for mass dispersion and electrostatic analyzers (ESA) to compensate for energy dispersion inherent in inductively coupled plasma and secondary ion sources. (a) Forward geometry where the magnetic sector precedes the ESA and (b) reverse geometry where the ESA precedes the magnetic sector (Modified after Fig. 3 of Ireland (2013))

obtaining the high-precision measurements required for geochronological studies when using plasma source instruments or ion microprobes; however, an ESA is not required for thermal ionization instruments (see descriptions of different mass spectrometers below).

Other types of tandem geometries have been employed, including double- or triple-focusing designs with multiple magnetic sectors (de Hoffman 1996). These designs result in increased abundance sensitivity and high selectivity but suffer from increased complexity, cost, and transmission losses.

Ion Detection

Two general types of detectors are commonly used to measure ion-beam intensity. For large beam currents up to 10^{-10} A, a deep, narrow faraday cup positioned behind the collector slit captures the incoming ions. The incident ions are neutralized by electrons from the ground that flow through a large resistor (10^{10} – 10^{12} Ω). The potential across the resistor is amplified and read by a digital voltmeter. Signals of several millivolts up to 50 V can be reliably measured using faraday cups.

At lower ion beam currents, electrical noise becomes a substantial component of the total signal present in the cups. In order to measure beam currents smaller than about 10^{-13} A, collectors that use signal multiplication are needed. The two types most commonly employed are Daly detectors and secondary electron multipliers (SEMs). A Daly detector consists of a polished metal “knob” placed under a large negative potential (Daly 1960). Incoming positively charged ions are attracted to the knob and, upon impact, release a shower of secondary electrons. These electrons are accelerated toward a nearby positively charged phosphor screen where they generate light pulses that are amplified and measured by a sensitive photomultiplier. SEMs consist of either discrete-dynode or continuous-dynode (channeltron) designs that rely on secondary electron emission after initial collision of an ion on the dynode surface (Allen 1947; Poenisch 1976). Release of additional electrons causes a cascade effect, multiplying the initial collision by gain factors of 10^4 – 10^8 (Gross 2011). Electrical output for Daly and SEM detectors is typically given in counts per second that must be calibrated (at least at the upper end of the range) against voltages produced for the same beam on a faraday cup.

Charge-coupled device (CCD) detectors, a relatively new type of silicon-based electronic device capable of detecting multichannel arrays of electromagnetic radiation, are capable of measuring impinging ion currents and have been used as detectors on miniaturized spectrometers (Sinha et al. 2011). However, these detectors have not yet been incorporated into instruments used for high-precision geochronological work.

Data Collection

Data collection in modern computer-controlled mass spectrometers involves measurement of multiple scan cycles in order to attain high-precision results. Single-collector instruments require magnet cycling from low to high-mass, counting intensities at each mass (and background positions) before returning to the low-mass peak to repeat the cycle. This form of analysis is referred to as dynamic peak-jumping mode and requires stable ion beam intensities to achieve precise isotope ratios. Multicollector instruments running in static mode do not require changes in magnet current and can therefore tolerate short-term beam instability because ion beams for all masses of interest are measured simultaneously. Static multicollection methods still gather data in separate blocks that allow statistical treatment and correction for instrument drift and beam growth or decay. However, static multicollection requires that corrections for electronic biases between detectors and amplifiers must be made by running collector gain calibrations with some frequency. Alternatively, high-precision measurements can be made on multicollector instruments using a multi-dynamic analysis

Table 1 Distribution of masses steered to different collectors that have been positioned at single atomic mass unit spacing for three types of data collection (dynamic peak jumping, static multicollection, and multi-dynamic triple jumping) for Sr-isotopic compositions (^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr) while monitoring ^{85}Rb to correct mass 87 for ^{87}Rb

Analysis type	Magnet jump	Collector number						
		Lo-3	Lo-2	Lo-1	Axial	Hi-1	Hi-2	Hi-3
Dynamic peak jumping	1	–	–	–	84	–	–	–
	2	–	–	–	85	–	–	–
	3	–	–	–	86	–	–	–
	4	–	–	–	87	–	–	–
	5	–	–	–	88	–	–	–
Static multicollection	1	–	–	84	85	86	87	88
Multi-dynamic triple jumping	1	–	–	84	85	86	87	88
	2	–	84	85	86	87	88	–
	3	84	85	86	87	88	–	–

that involves double or triple magnet jumps that measure the same isotope ratios in sequential sets of collectors. This method is capable of canceling out beam growth or decay, correcting for collector/amplifier bias, and applying a power law mass fractionation correction. An example of these three types of data collection schemes intended to determine the isotopic composition of Sr is shown in Table 1. Total length of analysis time depends on signal intensity and desired precision but can take from a few minutes to several hours for the highest-precision results. A variety of other corrections are necessary to produce the most precise and accurate data including baseline subtraction, detector linearity, and isobaric interference.

Mass Resolution

One of the main performance considerations in mass spectrometry is the ability of an instrument to distinguish two peaks having different mass-to-charge ratios. This is easier for lower-mass elements where differences in isotope masses are large relative to total mass, but becomes increasingly difficult for high-mass elements or for different species having similar masses (for instance, ^{29}Si vs. $^{28}\text{Si}^1\text{H}$ or ^{87}Rb vs. ^{87}Sr). Mass resolution is specified as the overall mass under consideration divided by the difference between masses being considered ($m/\Delta m$). For instance, a mass spectrometer needs a mass resolution of only 87 to resolve ^{86}Sr from ^{87}Sr ($87/[86.9089-85.9083]$) but a value of about 3,500 to resolve ^{29}Si from $^{28}\text{Si}^1\text{H}$ ($29/[28.9765-28.9848]$) and more than 200,000 to resolve ^{87}Rb from ^{87}Sr ($87/[86.9092-86.9089]$). Modern magnetic sector mass spectrometers have mass resolutions ranging from 300 to more than 5,000.

Mass resolution can be determined by noting the Δm for the closest spacing of two, equal-intensity peaks separated by a minimum signal less than a specified fraction of peak height (typically 10 % or 50 %). A more common and easily measured determination of mass resolution uses the width of a peak (in Δm) measured at a stated fraction of the peak height (commonly at 1 %, 10 %, or 50 %, the latter of which yields full width at half maximum, or FWHM; Fig. 4). Ideally, peaks obtained by scanning the ion beam across the collector slit will have flat tops and steeply sloping sides that allow minor mass drift without affecting ion beam intensity. Width at the base of the peak is approximately the sum of the widths of the source and collector slits, whereas the width of the peak flat is related to the ratio of the collector slit width to the ion beam width. A narrower collector slit will result in higher mass resolution, but will reduce the width of the peak flat. Reducing the

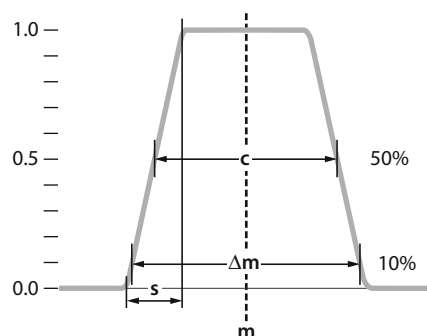


Fig. 4 Schematic depiction of an instrumental scan across an isotope of mass m , showing a trapezoidal-shaped peak with a flat top at a fractional intensity of 1 (*thick, gray line*). Peak width measured at 50 % of the peak height represents the collector slit width (c) and the width of the peak slope (s) represents the width of the demagnified source slit. Mass resolution at the 10 % peak height is given by $m/\Delta m$ (Modified after Fig. 6 of Ireland (2013))

width of the source slit will also result in higher mass resolution along with increased peak flat, but will cause a reduction of ion beam transmission. Therefore, mass resolution is often a compromise between the ability to effectively separate peaks with similar masses and the ability to acquire high-precision isotope data from those peaks.

A concept related to mass resolution is the amount that the tail of one peak may contribute to the signal of an adjacent peak. This measure is called abundance sensitivity and represents the ratio of the maximum ion current measured at a specified mass divided by the maximum ion current present for the same species measured at an adjacent mass. It is commonly measured at mass 237 (no natural isotope) while running a large ^{238}U signal. Tails arise from collision of ions in the flight tube with residual gas molecules resulting in a loss of energy and a shift toward the lower-mass side of the peak. Abundance sensitivity is therefore related to the quality of the vacuum in the instrument. Flight tube pressures in the low 10^{-9} mbar range commonly yield abundance sensitivities of ~ 0.000002 (2 ppm), although this can be improved by up to two orders of magnitude by addition of an energy filter in front of the collector or by designs incorporating multiple magnetic sectors.

Chemical Separations

In order to reduce the number of isobaric interferences and to improve precision and reproducibility of the measurements, samples used for geochronological purposes are commonly reduced to pure chemical forms using cryogenic separation for noble gases (Ar) or liquid chromatography after acid digestion for solids. Only the purified elements of interest are then introduced into the ion source of the mass spectrometer, reducing or eliminating interferences associated with complex matrices typical of geologic material. Consequently, mass resolution requirements are simplified to unit mass differences, and isobaric interferences from combinations of lower-mass molecules are dramatically reduced.

Chemical separations are usually performed under cleanroom conditions involving highly filtered airflow and the use highly refined reagents. Cleanroom conditions are designed to reduce the potential contaminants added during processing, which in turn results in reduced amounts of materials not present in the original sample (known as “blank”). Low chemical processing blanks allow more accurate analysis of substantially smaller-sized samples, which facilitates dating of rocks using isochrons derived from mineral separates, or when total sample size is very limited. Analysis of solid materials (rocks and minerals) requires quantitative digestion using high-purity

hydrofluoric, nitric, and hydrochloric acids. Complete dissolution of a known amount of sample allows the addition of a “spike” consisting of a solution containing a known amount of purified tracer isotope. Once the tracer is isotopically equilibrated with the sample, it can be used to monitor and correct for mass fractionation that occurs during the isotope analysis or for quantifying the concentration of the element of interest in an unknown through a procedure known as isotope dilution (Dickin 2005; Faure and Mensing 2005).

Mass Spectrometry Used for Dating

Principles described above are common to a variety of mass spectrometers used to collect isotope ratios for geochronological purposes. The following groupings are largely based on differences in how ions are produced. Comparisons between these mass spectrometric methods applied to radiogenic elements used for dating rocks and minerals can be found in a number of textbooks and review articles (Goldstein and Stirling 2003; Faure and Mensing 2005; Dickin 2005; Siebel and van den Haute 2007; Ireland 2013).

Thermal Ionization Mass Spectrometry

Thermal ionization mass spectrometry (TIMS) relies on thermal energy to produce ions from a sample placed on a thin ribbon (filament) of a highly purified refractory metal. Solid samples are prepared by acid digestion followed by chemical separation processes that are specific to the individual elements of interest. After separation, the resulting purified salt is loaded as a small drop of liquid onto a filament of rhenium, tantalum, or tungsten, either by itself or along with an activator such as Si-gel, Ta-oxide, or carbon suspension that helps stabilize or enhance ion emission. Depending on the ionization characteristics of a given element, samples can be loaded onto a single filament that produces both evaporation and ionization or on double- or triple-filament assemblies where separate filaments control evaporation and ionization. Loaded filaments are placed in the TIMS source, which is evacuated to pressures of $\sim 10^{-8}$ mbar, and then heated by passing a current of about 1–5 A. Heating under these conditions yields filament temperatures of 800–3,500 °C, which is sufficient to cause sample evaporation and at least partial ionization of a number of elements. Ions are extracted from the evaporation cloud in front of the filaments and accelerated through the source optics into the mass analyzer (Fig. 5a).

TIMS analyses of natural, nonvolatile radioactive isotope systems have been the historical standard in geochronology studies for more than 60 years. This includes dating systems such as U-Pb, Rb-Sr, Sm-Nd, and more recently Lu-Hf, Re-Os (in negative-ion mode), and U-Th disequilibrium studies. Advantages of TIMS analyses are in part derived from the careful chemical preparation which reduces mass-resolution requirements. The fact that different elements evaporate at different temperatures can also be used as an advantage for eliminating unwanted interferences to a certain extent (i.e., removal of ^{87}Rb at low temperature prior to analysis of ^{87}Sr at higher temperature) or for combined runs from the same filament (i.e., single-grain zircon or opal dating with no chemical separation where Pb data are collected at low temperature, U at intermediate temperature, and Th at high temperature). Thermal ionization also results in ions with a low energy spread allowing TIMS instruments to be relatively simple, relying only on single-focusing designs (magnetic sector). The main disadvantage of TIMS is that many elements have low to very low ionization efficiencies resulting in detection of only a small fraction of the total atoms present on the filament. Variations in matrix composition can also affect sample chemistry, resulting in poor ionization for impure separates. These shortcomings can be overcome by improving chemical

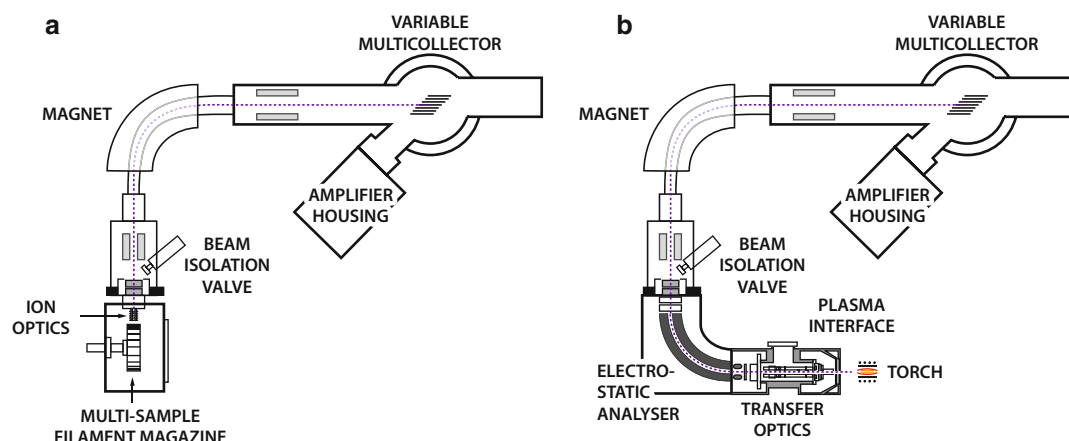


Fig. 5 Schematic diagram depicting designs of modern commercially available magnetic sector instruments consisting of a single-focusing solid-source thermal ionization mass spectrometer (**a**), and a double-focusing inductively coupled plasma mass spectrometer with forward geometry (**b**). Note that the two instruments are identical past the beam isolation valve (Diagrams courtesy of Thermo Fisher Scientific, Inc.)

separations and, in some cases, by adding an enhancer to the filament along with the sample load to increase the ionization efficiency without adding blank. TIMS analysis times are lengthy (several hours to obtain the highest-precision results), and total throughput can be low due to arduous chemical preparations.

Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma–mass spectrometry (ICP–MS) uses a plasma source utilizing Ar as the plasma support gas (Fig. 6). A Fassel-type torch with automated radio-frequency matching allows the aerosol gas to punch a hole through the plasma. The Fassel torch uses relatively low gas flow and can be used for aqueous samples using either a peristaltic pump or Meinhard nebulizer, or, for “dry” samples from which most of the liquid has been removed, by desolvation using a microconcentric nebulizer. The nebulizer converts the solution into an aerosol that, while passing through the plasma source, is desolvated, dissociated, and ionized. The interface region of the instrument usually consists of two cones, separated by a very small distance that is being pumped by a rough pump. The whole interface region is made from material that dissipates heat easily such as copper or aluminum that is also cooled by circulating chilled water to reduce the effects of the high-temperature plasma (up to 8,000 °K) on the cones. The first cone, known as the sampler cone, typically has an orifice of 0.8–1.2 mm internal diameter, while the second cone, the skimmer cone, has a much smaller orifice (0.4–0.8 mm). The cones are usually made of Ni, although different materials, such as Pt, can be used depending on the element being ionized and the aggressiveness of the matrix. The role of the interface region is to transport the ions efficiently, consistently, and with electrical integrity from the plasma, at atmospheric pressure, to the mass spectrometer analyzer region, where pressure is at $\sim 10^{-7}$ or $\sim 10^{-8}$ mbar. When the ions emerge from the skimmer cones, they are directed through the ion optics that will focus the beam into the analyzer region of the mass spectrometer (Fig. 5b).

The advantage of the ICP source is that it can ionize nearly all elements in the periodic system, and when combined with a multicollector system as described above, it allows for the measurement of isotopic compositions of many more elements than TIMS methods, especially those that are difficult to ionize by thermal methods. This opened up the analysis of many useful systems in geochronology,

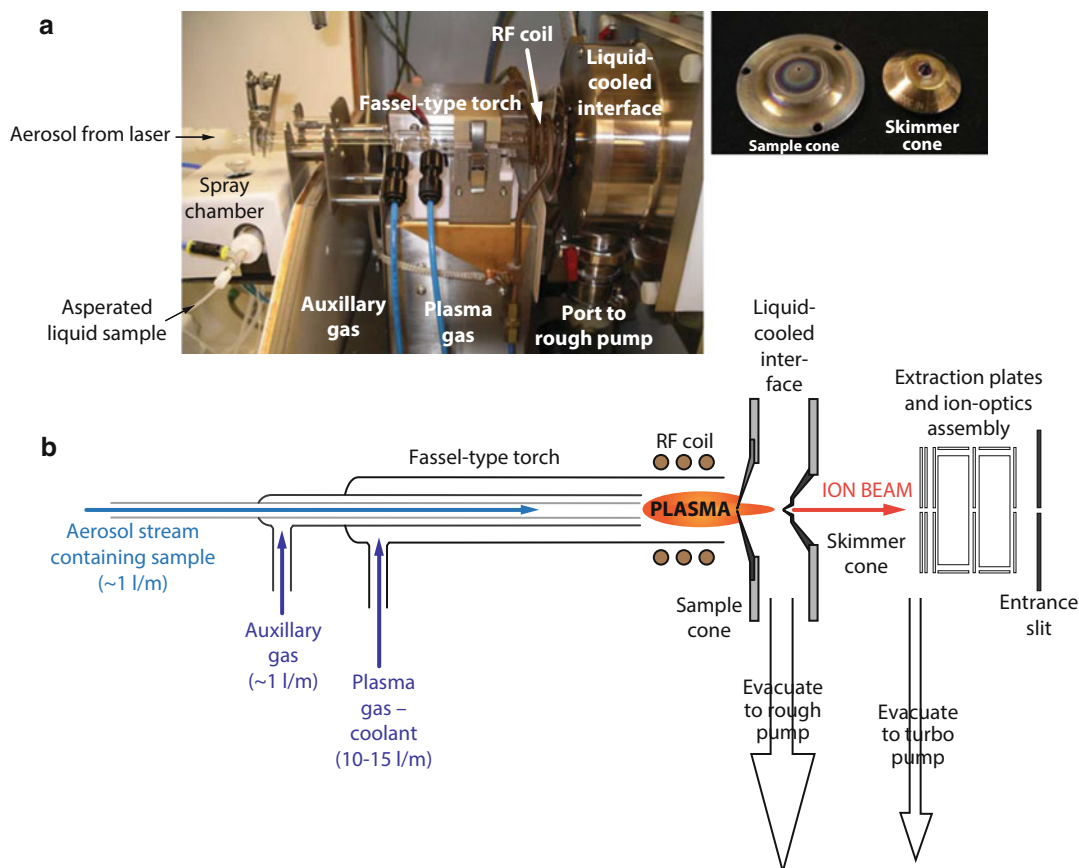


Fig. 6 (a) Photograph of the source area of an inductively coupled plasma mass spectrometer showing the layout of major components (*left*) and the sample and skimmer cones (*right*) which are attached to the liquid-cooled interface. (b) Schematic diagram of the main components shown in photograph (a)

such as Al-Mg, Fe-Ni, Mn-Cr, Pd-Ag, and Hf-W as well as allowing for more precise analysis of Hf and Pb isotopic compositions.

The ICP source can also be coupled to a laser ablation (LA) system that allows in situ production of ions while imaging the sampling process (Košler and Sylvester 2003; Longerich 2008; Koch and Günther 2011). LA-ICP-MS has been used extensively for U-Pb dating of zircons, as well as on other mineral matrices when a detailed understanding of sample texture and composition is required. Laser ablation adds more complexity to ICP-MS systems such as the effects of laser wavelength and pulse length on formation of aerosols, processes of elemental fractionation during lasing and in the vapor stream, adequacy of reference materials and calibration of the system using age standards, sampling strategies and analytical protocols, and data collection and reduction strategies (see numerous chapters in Sylvester 2008). Despite these complexities, LA-ICP-MS represents a successful and powerful dating tool with a growing number of applications.

There are strong matrix effects in ICP-MS that tend to reduce the reproducibility and accuracy of the analysis. To overcome this disadvantage, the element of interest can be carefully separated from its matrix through ion exchange while insuring a maximum yield (>95 %) through the process. The major limiting factor on the precision of multicollector-ICP-MS isotopic analyses stems from the instability of the plasma. An ESA is used to clean up the energy dispersion inherent in the plasma source and make it match the dispersion of the sector analyzer. In addition, mass fractionation associated with ionization in the ICP source is significantly larger than that observed in TIMS.

However, instrument-induced mass biases are usually constant during the analyses allowing for proper correction, either by sample-standard bracketing or by the addition of another element of comparable mass range such as Tl to monitor Pb mass bias. Finally, because the ICP source is capable of ionizing all constituents introduced into the plasma, corrections for spectral interferences that may overlap the masses of interest must be made.

Noble Gas Mass Spectrometry

Radiogenic noble gases including ^4He and ^{40}Ar can reside within certain minerals over geologic time scales and are often used in research applying geochronology and thermochronology. Noble gas mass spectrometry requires extraction and purification of exceedingly small fractions of gas from mineral grains under ultrahigh vacuum systems and is generally done using a high-temperature furnace or infrared laser. Heating can be done incrementally, such that gas fractions having different isotopic compositions can be separated. In some cases, step heating may provide information constraining the thermal evolution of the sample. Gases released from minerals during heating are isolated using chemical and cryogenic traps. The noble gas of interest is introduced into a gas-source mass spectrometer through an inlet port. Positive ions are created when the gas interacts with a heated filament causing ejection of an outer electron, and the resulting ions are accelerated through the source optics into a single-focusing magnetic sector mass spectrometer. The noble gas isotopes are typically measured in static mode.

Secondary Ion Mass Spectrometry

Secondary ion mass spectrometers (SIMS) were developed to provide in situ elemental and isotopic compositions on samples at high spatial resolution (Ireland et al. 2008). To do this, a primary beam of energetic ions is focused onto a small spot on the sample (typically 10–50 μm). Bombardment of the sample surface causes ablation and generates a variety of metal ions and more complex species that can be extracted to form a secondary ion beam. Chemically active elements, such as O^- and Cs^+ , are most commonly used for the primary beam because of their enhanced ability to generate secondary ions. Because secondary ions generated in this manner have a large range of both energies and mass-to-charge ratios, SIMS instruments employ a dual-focusing design with either forward or reverse geometries (Fig. 3). They also require high-mass resolution in order to discriminate between numerous secondary ion species that may have similar masses. To accomplish this, these instruments employ large magnetic and electrostatic sectors and long flight paths.

In the last 30 years, SIMS analyses of the U and Pb isotopic compositions of zircon have become a critical tool for dating igneous and metamorphic rocks and for providing age data used in sedimentary provenance studies. Although individual ages are not as precisely determined as those analyzed by TIMS, SIMS has the distinct advantage of being able to analyze distinct spatial domains within a single grain that may be related to separate geological events. Furthermore, in situ SIMS analyses eliminate the involved and time-consuming step of chemical processing required by TIMS. Additional elements can be added as part of the same SIMS spot analysis (i.e., rare-earth and high-field-strength elements in zircon) allowing petrologic interpretations to accompany age data (petrochronology). Other minerals besides zircon have been dated using SIMS by both U-Pb and U-series methods (monazite, xenotime, titanite, baddeleyite, rutile, and opal). Unlike LA-ICP-MS, the SIMS primary beam is used both to sample the target and to simultaneously generate ions from resulting volume. The SIMS “sputtering” process is much less aggressive than vaporization via laser ablation and evacuates sample volumes that are only several micrometers rather than several tens of micrometers deep. Consequently, SIMS analyses require longer data acquisition times but are less likely to incorporate zones of disparately aged material at depth. Mass-dependent fractionation is

also less pronounced in SIMS analyses, and isotope ratios require less elaborate correction procedures.

Summary

Over the last 100 years, mass spectrometry has become a critical aspect of geological science by providing ages from isotope–ratio measurements of natural radioactive decay. Mass spectrometry has also provided isotopic compositions of a myriad of solids, liquids, and gases that have been invaluable for understanding earth science processes, the rates at which they occur, and the characterization of the compositions of numerous geochemical reservoirs.

Mass spectrometry is based on the principle that charged particles moving through electromagnetic fields are affected in ways that allow the dispersion of ions of different masses into separate signals that can be measured independently. All mass spectrometers consist of three main components: (1) a source of ions and a means of imparting velocity, (2) a mass analyzer that separates the moving ions on the basis of their mass-to-charge ratios, and (3) a collector system that can quantify the intensity of separated ion beams. Most mass spectrometers used for geochronological studies must be able to produce high-precision isotope–ratio measurements of stable ion beams and therefore make use of a magnetic sector mass analyzer. Because it is possible to generate ions and introduce them into the mass analyzer by various means, several types of mass spectrometers have been developed. These instruments can provide precise and accurate measurements on a wide range of isotope systems using a spectrum of different materials and analytical strategies.

Cross-References

- Accelerator Mass Spectrometry
- Helium Isotope Dating
- Historical Development of Dating Methods
- Laser Ablation–Inductively Coupled Plasma Mass Spectrometer (LA–ICPMS)
- Lutetium–Hafnium Dating
- Potassium–Argon and Argon–Argon Dating
- Rhenium–Osmium Dating
- Rubidium–Strontium Dating
- Samarium–Neodymium Dating
- Secondary Ion Mass Spectrometer (SIMS)
- Thermal Ionization Mass Spectrometer (TIMS)
- Uranium–Series Dating
- Uranium–Lead Dating
- Uranium–Thorium–Helium Dating

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Sea Level Change (U-Series)

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Synonyms

Quaternary sea level change; Sea level variations; U-series disequilibrium dating; U-Th dating

Definitions

U-series dating: A method for determining the age of material based on the changes in amounts of various isotopes within the decay chains of uranium-238 or uranium-235 due to radioactive decay.

Sea level change: Changes in global mean ocean level over time, usually associated with climatic changes.

Introduction

One of the most dramatic applications of uranium-series dating has been the quantification of past changes in late-Quaternary global sea level through U-Th dating of fossil corals and speleothems (cave deposits). Large-scale changes in Quaternary sea level result from changes in the volume of ice on land associated with the ice ages. This is because the water that formed the great ice sheets of past glaciations came from the ocean. As sea level changes, the location and elevation of coral growth and speleothem formation in coastal caves also must change.

Corals make excellent indicators of sea level because reef forming corals require sunlight and so must grow near the sea surface. A typical coral reef has a reef crest; behind the crest is the back reef or lagoon, and in front of the crest is the fore reef that slopes down into deeper water. Reef-crest corals make excellent sea level markers, such as *Acropora palmata* in the Atlantic Ocean (Goreau 1959), which grows predominantly within a few meters of the sea surface. In the Pacific Ocean, it is more common to have an assemblage of corals that indicate growth on a reef crest (Huston 1985). When a coral reef becomes exposed on land, either due to dropping sea level or tectonic uplift, the reef becomes a terrace, with the reef crest forming the lip of the terrace. Many fossil coral terraces around the world have been sampled and dated with U-series techniques, resulting in data that forms the backbone of our record of Late-Quaternary sea level (see references in Medina-Elizalde 2013).

Speleothems also help to constrain past sea level changes. Speleothems are cave deposits, many of which formed from water flowing or dripping into vadose cavities. Caves often form in bedrock near sea level because of the corrosive quality of the groundwater where fresh water meets sea water. When these caves are exposed to air and dripping water after sea level falls, speleothems form. When sea level rises and floods the cave again, speleothems stop growing. The growth of speleothems in these types of caves thus means that sea level was below the elevation of the cave at the time the

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speleothem grew. Dating such speleothems with U-series methods provides a history of periods during which sea level was below a certain elevation (see references in Edwards et al. 2003).

Vertical movement caused by tectonic forces can cause fossil corals and speleothems to be moved from their original elevation. This can be an advantage, such as when tectonically uplifting coastlines cause corals or speleothems that grew below modern sea level to be exposed on land and more easily sampled.

Obtaining sea level information from a fossil coral or a speleothem deposit requires knowledge of the deposit's elevation and age. If the deposit is on a tectonically stable substrate, then the measured elevation indicates the elevation of sea level when the deposit was formed. If the deposit is on a tectonically active substrate, then one must correct the measured elevation for the amount of tectonic movement that occurred since the deposit was formed. The tectonic uplift or subsidence rate is needed for this correction and is usually determined by measuring the elevation of a deposit that was formed at a known elevation in the past. For sea level studies, the deposits formed during the last interglacial period, when sea level was ~6 m higher than present (Kopp et al. 2009), are often used to determine tectonic uplift or subsidence rates. Local sea level can also vary due to changes in the shape of the earth (called isostatic changes) due to changes in the weight of the ice sheets and the oceans resulting from the ice ages.

U-Th dating can provide precise age determination of fossil corals and speleothems. The precision in ages is important not only because it determines the precision of the sea level record but also because the sea level record is used to test the current theory for the cause of the ice ages, the Milankovitch Theory (Milankovitch 1941). This theory states that the ice ages wax and wane due to the amount of solar insolation reaching 65° N latitude. When summer insolation is low, ice will build up from year to year, causing a glaciation. When summer insolation is high, ice will melt, causing an interglacial period. The changes in summer solar insolation at 65°N are caused by changes in the orbit of the Earth around the sun. These changes can be calculated with a precision of about 1 ka (1,000 years) (Berger 1978). To test the Milankovitch Theory, it is necessary to date geologic records of the ice ages to a similar or better precision.

Dating Systematics and Analytical Methods

U-Th dating is based on the radioactive decay products of ^{238}U : ^{234}U and ^{230}Th . ^{234}U has a half-life of 245,250 years and ^{230}Th has a half-life of 75,690 years (Cheng et al. 2000). Uranium is weathered out of the continental rocks, and because it is soluble, it is transported through surface waters to the oceans. Thorium is also weathered out of continental rocks, but because it has very low solubility in natural waters, it has very low concentrations in most water on Earth. When corals grow in the ocean, they incorporate approximately 3 µg/g of U into their skeleton, which is made of the mineral aragonite. When speleothems crystallize from dripping water, they incorporate U also, though the concentration is much more variable. Thorium produced by the decay of uranium is essentially absent from corals and speleothems due to its very low solubility, unless the sample has incorporated clay-rich or organic-rich sediments, which can have significant amounts of thorium in them. After the coral or speleothem forms, the uranium in these deposits will decay, producing ^{230}Th . The amount of ^{230}Th increases at a predictable rate with time, providing a chronometer. Ages calculated from the ingrowth of ^{230}Th are called ^{230}Th ages, which can, in principle, be used to date materials as young as 3 years and as old as 600,000 years (Edwards et al. 1987; Edwards 1988). There is also

a chronometer based on the decay products of ^{235}U (present in all uranium in a ratio of 1 part ^{235}U to ~138 parts ^{238}U), which includes ^{231}Pa (protactinium) with a half-life of 31,000 years (Cheng et al. 1998). Protactinium has very similar chemical properties to thorium, and so the ingrowth of ^{231}Pa in a sample provides a chronometer. Ideally, the ^{230}Th and ^{231}Pa ages on the same sample should be the same (often called concordant) within error. ^{231}Pa ages are not commonly available because the measurements are difficult to make.

For fossil corals, the isotopes ^{234}U and ^{238}U are also important. When uranium is weathered from the continents, the ^{234}U atoms are dissolved more easily because their chemical bonds have been damaged by the radioactive decay process. This means that the oceans have a higher activity ratio (atomic ratios normalized by the ratio of their decay constants) of ^{234}U to ^{238}U than they would have due to decay in a chemically closed environment. The ^{234}U to ^{238}U activity ratio due to the long-term decay process is 1.000 (i.e., in secular radioactive equilibrium), whereas the ratio in the ocean water is 1.147. The activity ratio of ^{234}U to ^{238}U is often expressed as $\delta^{234}\text{U}$ in delta units ($\delta^{234}\text{U}_{\text{sample}} = [({}^{234}\text{U}/{}^{238}\text{U}_{\text{sample}} \div {}^{234}\text{U}/{}^{238}\text{U}_{\text{standard}}) - 1] \times 1,000$, where ${}^{234}\text{U}/{}^{238}\text{U}_{\text{sample}}$ and ${}^{234}\text{U}/{}^{238}\text{U}_{\text{standard}}$ are expressed as activity ratios and ${}^{234}\text{U}/{}^{238}\text{U}_{\text{standard}}$ is equal to the secular equilibrium value of 1.000). The modern ocean $\delta^{234}\text{U}$ value is 147 ± 1 per mil (‰) (Stirling and Andersen 2009). Evidence suggests that this ratio has remained relatively constant during the last 400,000 years (Henderson et al. 1993), consistent with the long time that uranium resides in the ocean. The ^{230}Th age of a fossil coral can be used to calculate the initial $\delta^{234}\text{U}$ value. How closely the value matches the modern ocean value provides a measure of the coral's quality of preservation.

Analytical methods for measuring uranium and thorium isotopes have improved dramatically since the first ^{230}Th ages were measured in the 1950s (Barnes et al. 1956). The first ages reported were measured using alpha counting techniques, where the alpha particles given off during radioactive decay were detected and counted. A typical measurement of a 125,000-year-old (last interglacial age) sample had a precision (2σ) of 10,000–20,000 years in age and 20–40 per mil in $\delta^{234}\text{U}$ value. Thermal ionization mass spectrometry (TIMS) replaced alpha counting as the preferred method of analysis in the late 1980s. TIMS methods involve measuring atoms of the various uranium and thorium isotopes rather than just those that decay during the measurement period using heat to ionize the atoms, a sector magnetic analyzer to separate the isotopes by mass, and a secondary electron multiplier to measure the ions collected (Chen et al. 1986). A typical measurement of a 125,000-year-old sample had a precision of 500–2,000 years in age and 1.5–8 per mil in $\delta^{234}\text{U}$ value. Magnetic sector inductively coupled plasma mass spectrometry (MS-ICPMS) became the preferred method of analysis in the late 1990s (Shen et al. 2002). This method differs from TIMS in the manner in which the isotopes are ionized before being separated by the magnet. ICPMS uses a very hot gas (plasma) to ionize the sample, which is introduced into the plasma as a liquid nebulized into tiny droplets. The precision ranges from 300 to 1,000 years for a 125,000-year-old sample and 1–3 per mil in $\delta^{234}\text{U}$ value. The greater ionization efficiency of the plasma results in a higher percentage of ions reaching the collector and the increase in precision relative to TIMS measurements. The sample size in this technological progression decreased from grams to 10s of micrograms, and the time involved decreased from weeks of counting decays to hours of counting atoms. There is also the option of using large samples (grams) to run samples on MS-ICPMS with very high intensities, where the ions are measured on faraday cups instead of a secondary electron multiplier, which results in precisions of 100–200 years for 125,000-year-old samples and 0.2 per mil in $\delta^{234}\text{U}$ value (Stirling and Andersen 2009; Cheng et al. 2013).

Preservation and Location

Fossil corals from all over the world have been collected and analyzed. Initially, all data were considered exciting and encouraging, as the timing of high sea level events was found to match the predictions of the Milankovitch Theory (Broecker et al. 1968). As more corals were analyzed and the precision of the measurements improved, it became clear that many of the samples had been altered such that their uranium and thorium isotopic composition did not provide a perfect clock.

There are two main indicators of alteration in fossil corals. One is the presence of calcite, which has the same chemical formula (CaCO_3), but a different arrangement of atoms, than aragonite. Calcite is the more stable configuration of atoms of the two minerals. Rain water percolating down into the fossil coral reef can cause the rock to dissolve and reprecipitate, often resulting in a change from aragonite to calcite. Calcite accommodates less uranium in its structure than aragonite, so it is likely that recrystallization causes a disruption of the uranium-series isotopes in the fossil coral. Samples are often measured for calcite content prior to uranium-series analysis to avoid measuring altered samples. The second indicator is an initial $\delta^{234}\text{U}$ value that is higher than the modern marine value. Even with lower precision, early studies noted that many samples did not have initial $\delta^{234}\text{U}$ values near the modern value of about 150 but had values between 160 and 200, and a smaller number of samples had values well in excess of 200. The trend toward higher initial $\delta^{234}\text{U}$ values was noticed to be accompanied by a trend toward higher ^{230}Th ages in the late 1970s (Bender et al. 1979) and later quantified (Gallup et al. 1994). For every increase of 4 per mil in initial $\delta^{234}\text{U}$ value, the ^{230}Th age increased about 1,000 years in samples from Barbados, making it clear that some process was mobilizing uranium resulting in shifts in ages. Since this trend was quantified, many studies have adopted a cutoff for how far above the modern value the initial $\delta^{234}\text{U}$ value can be and still provide acceptable ages. This cutoff, or criterion, has varied from 0 (meaning that the initial $\delta^{234}\text{U}$ value must be within error of the modern value; Gallup et al. 2002) to 10 per mil (Medina-Elizalde 2013). As precision has improved, the initial $\delta^{234}\text{U}$ criterion has become more useful. Not all samples conform to this trend (e.g., data from New Guinea); data without these trends are much harder to evaluate. There are other methods to evaluate the quality of coral data, such as the uranium and thorium concentrations in the fossil coral and a holistic evaluation of the data set to see if it makes sense in terms of the geologic deposit.

Several workers noted that the observed trends in initial $\delta^{234}\text{U}$ value and ^{230}Th age are consistent with what might happen if the decay process itself caused the mobilization of uranium and thorium isotopes (Henderson and O’Nions 1995; Thompson et al. 2003). Most steps in the decay chain between ^{238}U and ^{230}Th are by alpha decay, where the equivalent of a helium atom is released during decay. Each time an alpha decay occurs, there is a physical movement called alpha recoil, where the atom can be dislodged from its site in the mineral structure. Thompson et al. (2003) used a mathematical model to show that alpha-recoil processes can produce the types of trends observed in Barbados corals and elsewhere. He further used the model to develop model ages, where the effects of this alteration can be corrected and produce a corrected ^{230}Th age. These model ages are very useful for checking a data set to see if the samples from a given deposit converge on a narrow age range when corrected, as alteration tends to spread the ^{230}Th ages out toward higher values. The model ages are only appropriate where the uranium and thorium isotopes display the type of trend produced by alpha recoil.

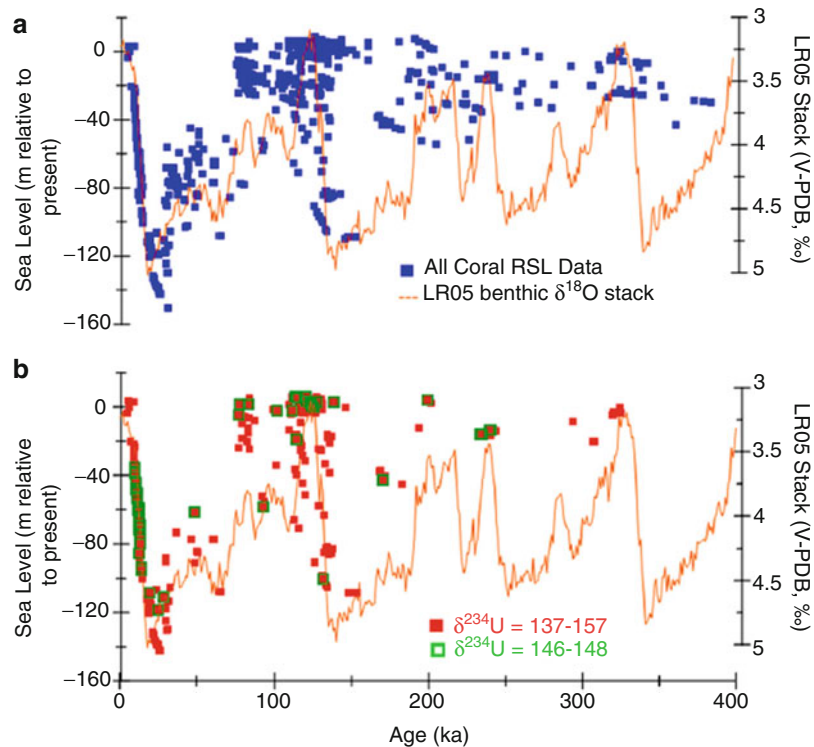


Fig. 1 Comparison between sea level elevation determined from fossil coral data and the stratigraphically continuous deep-sea oxygen isotope record (Lisiecki and Raymo 2005) spanning the last 400 ka (Reprinted from Medina-Elizalde (2013) with permission). Panel **a** contains all of the coral relative sea level (RSL) data in the compilation ($n = 897$) (blue squares). Panel **b** contains selected coral RSL data based on initial $\delta^{234}\text{U}$ values within the 137–157 ‰ (red squares) and 146–148 ‰ (green squares) ranges (See Medina-Elizalde (2013) for the references to data in this figure)

Late-Quaternary Sea Level Record from Fossil Corals and Speleothems

A recent compilation of three decades of work using uranium series dating of fossil corals provides a comprehensive documentation of sea level changes (Medina-Elizalde 2013). Much of the data for high sea level comes from locations with no to slow tectonic uplift, such as Barbados, Australia, the Bahamas, Hawaii, and Henderson Island (in the Pacific ocean), while much of the low sea level data comes from locations with high uplift rates, such as New Guinea, or from submerged samples obtained from ocean drilling, such as from Barbados and Tahiti. Figure 1a shows the data that has been collected, regardless of signs of alteration, superimposed on a record of deep-sea oxygen isotope changes as recorded by shells of foraminifera (Lisiecki and Raymo 2005). Because ice sheets preferentially incorporate light oxygen isotopes, the values of marine oxygen isotopes vary mainly as a function of ice volume. Sea level in the Late Quaternary also varies mainly due to changes in ice volume. Therefore, records of deep-sea oxygen isotopes and fossil coral sea level should reflect similar fluctuations.

It is clear from Fig. 1a that there is quite a bit of scatter and conflict in this graph of coral data. Figure 1b shows two applications of the $\delta^{234}\text{U}$ criterion, one in red with values accepted between 137 and 157 per mil and one in green with a much narrower range of 146–148 per mil. The strictest criterion reduces the number of data points significantly, but conflicting data points remain. One

conflict occurs during the last interglacial high sea stand (about 120,000–128,000 years ago) where multiple data sets suggest that sea level was higher than present, whereas data sets from New Guinea for this same period suggest a much lower sea level. The source of this discrepancy is unclear. The prevalence of data showing high sea level during the last interglacial period suggests that sea level did remain above the present value for most of the period. Another area of conflict is the many different sea level elevations reported for the high sea stand 80,000 years ago.

Despite these issues, the coral data generally follow the marine oxygen isotope record fairly well, with a few notable exceptions. The coral record suggests a much higher sea level around 80,000 years ago, a much longer last interglacial which remains high until roughly 115,000 years ago, and a much higher sea level 170,000 and 200,000 years ago. Model ages (Thompson et al. 2003) from the data that meet the 137 to 157 per mil initial $\delta^{234}\text{U}$ criterion do reduce the scatter in Fig. 1b (see Fig. 3b in Medina-Elizalde 2013), but do not remove the conflicting sea level data or change the relationship with the marine oxygen isotope record. The reasons for the scatter and conflicts in the data even after it has been screened for its initial $\delta^{234}\text{U}$ value and modeled to correct for alpha-recoil effects are likely many, including isostatic changes, uncertainties and/or inaccuracies in tectonic corrections, uncertainties in the water depth at which corals grow, and dating uncertainties and/or inaccuracies.

Medina-Elizalde (2013) performed a statistical analysis on the coral data that meet the 137–157 per mil initial $\delta^{234}\text{U}$ criterion to form a best fit record of sea level through time with a 95 % confidence level based on uncertainties in the sea level and the measured age. Figure 2a shows the results of this analysis superimposed on the data it is based on, and Fig. 2b shows the results superimposed on two, deep-sea oxygen isotope records (Lisiecki and Raymo 2005; Waelbroeck et al. 2002) and one oxygen isotope record from the Red Sea (Rohling et al. 2009). The coral sea level curve agrees broadly with the other sea level records. However, the coral record (a) shows higher sea level about 80,000 years ago, (b) does not show a drop between the last interglacial 125,000 years ago and the next high sea level event at about 100,000 years, (c) shows a high sea level about 140,000 years ago that is not present in the other records (though this is based on very sparse data), and (d) shows sea level much higher between 160,000 and 200,000 years ago (though this is based on very sparse data).

Edwards et al. (2003) assembled sea level data for the last 210,000 years (Fig. 3) based on speleothems and fossil corals that had an initial $\delta^{234}\text{U}$ within error of the modern seawater value and, where available, concordant ^{230}Th and ^{231}Pa ages. The data in Fig. 3 are connected by a line that is the best estimate (unlike the statistical method of Medina-Elizalde) of sea level based on the available data. For the sea level rise since the last glacial maximum 20,000 years ago, the line is based on drill core data from Barbados (not shown). For the period between 20,000 and 70,000 years ago, the line is based on an analysis by Chappell (2002) of ^{230}Th dates and coral terrace elevations from New Guinea. The speleothem data is shown with gray symbols accompanied by a downward facing arrow, indicating that the speleothem constrains sea level to have been below the plotted elevation. The speleothem data are generally consistent with the coral data, though the data at 200,000 years ago are only barely consistent within error. The estimated sea level records from Figs. 2 and 3 are very similar in overall shape and timing. There are some differences, as Fig. 2 has a higher estimate for sea level 80,000 years ago and 140,000 years ago and suggests a more detailed and variable sea level record between 80,000 and 130,000 years ago.

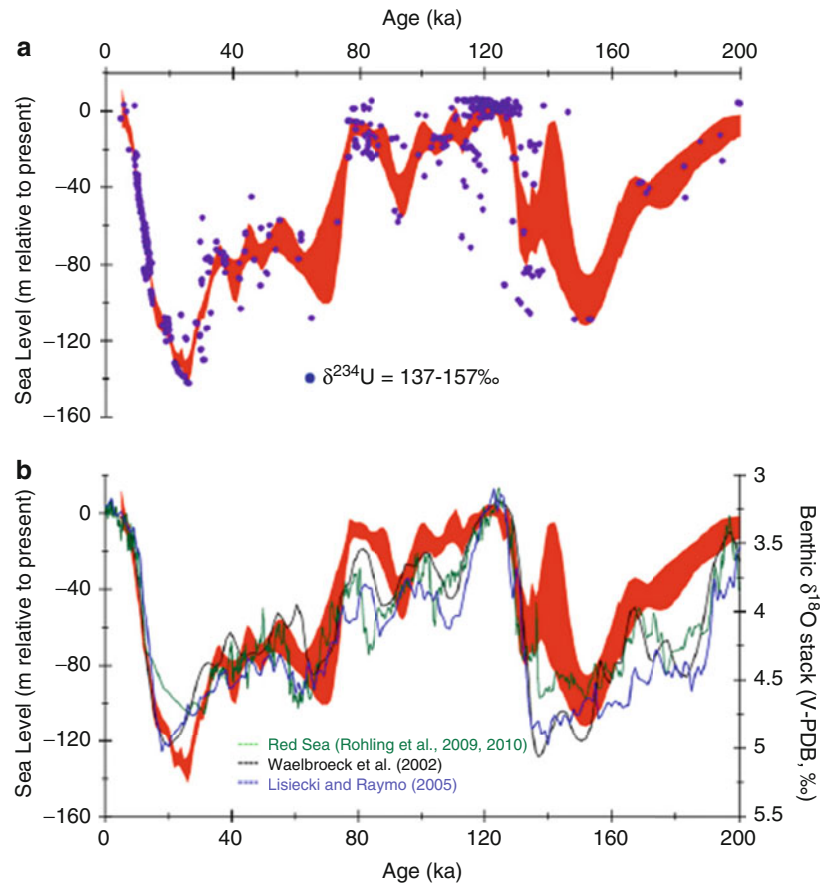


Fig. 2 Monte Carlo 95 % confidence intervals (*red curve*) based on sea level benchmarks calculated from samples having initial $\delta^{234}\text{U}$ values within the 137–157 % range. The Monte Carlo analysis is based on 1,000 runs and takes into account a sea level uncertainty of 6 m (1σ) and age uncertainties at a 2σ level (Reprinted from Medina-Elizalde (2013) with permission). The original coral RSL data used in this statistical analysis are also plotted (**a**, *blue circles*). The continuous sea level proxies are shown for comparison in (**b**) with references based on oxygen-isotope data as indicated in the figure

Finally, Fig. 3 makes it possible to evaluate how the uranium-series record of sea level compares with the timing of the orbital cycles that drive the glacial cycles according to the Milankovitch Theory. The peaks in the top curve in Fig. 3 are times when summers are warm in the northern high latitudes and when sea level should be high due to low glacial activity. While it is true that periods with high sea level almost always coincide with times of high 65°N summer insolation, it is also true that periods of high insolation do not necessarily result in high sea level. There are fewer low sea level data points, but what data there are show that low sea levels coincide with periods of low 65°N summer insolation. Thus, the uranium-series sea level data generally support the Milankovitch Theory for the ice ages. However, there are many unexplained relationships between the orbital cycles and the sea level data, such as the observation that higher 65°N summer insolation does not necessarily correspond to higher sea level and the observation that high sea level periods often continue well into periods of declining 65°N summer insolation.

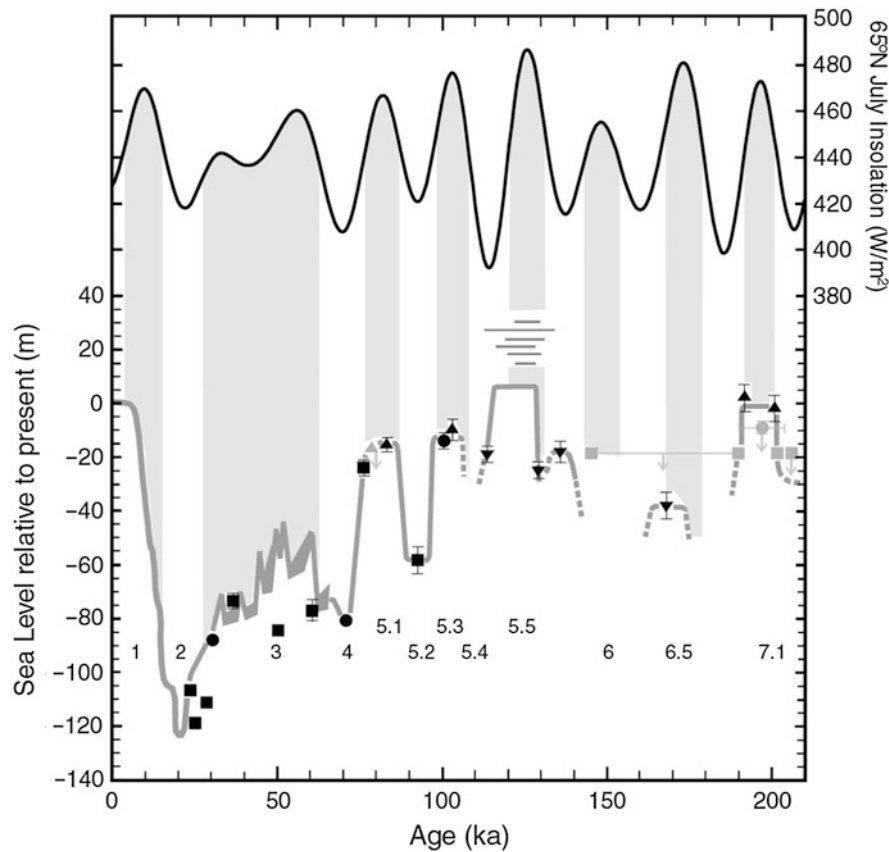


Fig. 3 Direct sea level data (210,000 years to present) from corals (*solid symbols*) and speleothems (*gray symbols*). The *gray symbols* represent maximum possible sea level based on speleothem growth. The marine oxygen isotope stages are indicated by numbers, where even numbers are glacial periods and odd numbers are interglacial periods. The line segments above the last interglacial high stand (125,000 years ago) are different estimates of the timing and duration of peak last interglacial sea level from corals and from direct dating of the marine oxygen isotope record. The placements of the line segments have no significance in terms of sea level elevation. The curve between 65,000 and 35,000 years is from Chappell (2002). Note that the curve disagrees with a $^{231}\text{Pa} - ^{230}\text{Th}$ concordant point at about 50,000 years. This indicates that either the curve or the point are in error, or that the curve does not capture the full range of sea level variability in this time range. July summer solar insolation at 65° north latitude is depicted in the top panel (Berger 1978). The vertical gray bars indicate times of high insolation and are intended as aids in comparing the curves

Cross-References

- Carbonates, Marine Carbonates, (U-Series)
- Carbonates, Speleothem Climatic, (U-Series)
- Mass Spectrometry
- Thermal Ionization Mass Spectrometer (TIMS)
- Uranium Series, Deep-Sea Sediment Dissolution Rate
- Uranium Series, Marine Sedimentation Rate
- U-Series Dating

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Thermal Ionization Mass Spectrometer (TIMS)

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A thermal ionization mass spectrometer (TIMS) consists of (1) an ion source (here a solid source), (2) a magnet (analyzer) that splits the ions depending on their mass to charge ratio (momentum filter), and (3) one or multiple collectors that measure the magnitude of the ion beams such that isotopic ratios of a given element can be computed (Nier-type spectrometer, Nier 1940).

Prior to analysis, a solution containing the purified sample is loaded on a metal filament (Re, Ta, Pt, or W) and dried down. In the evacuated source, ions are generated using the process of surface ionization by thermally heating the filament to ca. 1,200–1,800 °C. In a single-filament configuration, ions are directly emitted from the loaded sample; in a double- or triple-filament configuration, the sample is loaded on one or both of the side filaments where volatilization takes place followed by ionization using the center filament that is heated to a significantly higher temperature. Depending on the element, the use of various emitter substances can be used to enhance and stabilize the ionization. Most elements are analyzed as positive ions and some as negative ions (e.g., OsO_3^- , WO_3^-). Ionization efficiency depends on the work function of the filament material, the first ionization potential of the sample, and the temperature (Saha-Langmuir equation). Efficiencies range from 0.01 % (e.g., Hf) to ca 100 % (e.g., Rb) but are <1 % for most elements. The ionized portion of the sample is then accelerated and focused in a potential field (up to 10 kV) applied to an electrostatic lens stack (collimator) before entering the evacuated flight tube.

For large ion beams, the field of the magnet is typically held constant, and several masses are measured simultaneously using multiple collectors (static mode). For small ion beams, the magnetic field is typically cycled through the individual masses of a given element, which are measured sequentially using a single collector (dynamic mode, peak hopping).

Collectors include the following: (1) Faraday cups which accurately measure the current generated by an ion beam and therefore can be used in parallel; however, they require a significant noise correction and are thus only suitable for sufficiently large ion beams; (2) various types of multipliers (e.g., discrete or continuous dynode) for analysis of small ion beams, but in many cases, they are limited by a short life span and challenges involving intercalibration with other collectors.

A TIMS is often optionally fitted with an energy filter that results in a monoenergetic ion beam that enhances the abundance sensitivity by reducing tailing effects of major masses on adjacent minor masses.

The measured raw isotopic ratios must be corrected for the effects of mass fractionation and instrument-induced mass discrimination. The correction is typically between 1 % (for light elements) and 0.1 % level (for heavy elements) and can be done internally, using a known ratio of two or three isotopes (of either natural isotopes or added tracer isotopes) or externally by applying corrections observed on reference materials. In ideal cases isotopic ratios can be measured to a precision of <0.001 %.

Geochronometers that are commonly analyzed using a TIMS include U-Th-Pb, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os, and U-series disequilibrium.

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Cross-References

- ▶ [Lu-Hf Dating](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Rb-Sr Dating](#)
- ▶ [Re-Os Dating](#)
- ▶ [Sm-Nd Dating](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [U-series Dating](#)

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Thermochronology, Landform Evolution

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Definition

The use of thermochronometers having closure temperatures less than 200 °C that allow evaluation of the timing of geomorphic events or rates of landscape change caused by processes such as uplift, incision, exhumation, erosion, transport, and sedimentation.

Introduction

Continental topography links to some of the most fundamental questions about earth processes and history. Some modern topographic features, such as the Altiplano, Himalaya, or Tarim basin, are among the most striking physical features on the planet. Understanding the timing and processes that created these topographic spectacles would seemly provide profound insight into planetary dynamics. Topography is also central to interactions between a wide range of phenomena, including mantle circulation (e.g., Cazenave et al. 1989; Forte et al. 1993), ocean chemical evolution (e.g., Raymo et al. 1988), biota and biotic evolution (e.g., Dietrich and Perron 2006), and weather and climate on both local and global scales (e.g., Ruddiman and Kutzbach 1989; Molnar and England 1990). The ability to reconstruct paleotopography would lead to improved understanding of all these phenomena and their interactions.

Although thermochronology cannot directly constrain paleoelevation, it can provide estimates of the form, location, and scale of paleotopographic relief, as well as its change through time. Unique thermochronologic perspectives on paleotopography come from (1) spatial patterns of surface and subsurface cooling ages or cooling histories that reflect either spatially focused erosion (including incision) or the influence of topography on subsurface isotherm warping, and (2) the age-elevation relationship in paleolandscapes that may be preserved in the distributions of detrital cooling ages.

Low-Temperature Thermochronometers

Thermochronology begins with the measurement of ratios of isotopes, elements, or nuclear tracks that compose a parent-daughter radioisotopic decay system. These ratios reflect the thermal history of the sample in which they were measured. This is possible in commonly used thermochronologic systems because retention of the radiogenic (daughter) products, which “keep time,” varies inversely with temperature. A simple example is a bulk crystal parent-daughter ratio, which relates to age through a radioactive-decay equation. This age can be interpreted as the time elapsed since the crystal cooled below a critical temperature at which point daughter retention switched from nearly nil, due to diffusive or annealing loss, to essentially complete, due to a lack of thermal energy required to drive diffusion or annealing. This hypothetical temperature can be thought of as the

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closure temperature (T_c) (Dodson 1973), though in reality both the concept of closure and the mechanics of the increasing retentivity with decreasing temperature are more complicated. The thermochronometers used in studies about landscape evolution are called low-temperature thermochronometers and are characterized by closure temperatures or retentive zones cool enough to be impacted by valley incision or to be deflected by the Earth's surface topography. Widely used low-temperature thermochronometers include fission tracks and (U–Th)/He dating, both on apatite, which have closure temperatures of ~ 110 and ~ 70 °C, respectively.

In slightly more sophisticated applications, thermochronology involves measurement of a series of parent-daughter ratios and their inferred or observed distribution within a sample. This distribution reflects something more complex and potentially powerful about the thermal history of the sample and can be modeled as a finite time-temperature path, rather than a specific point in a monotonic cooling history. These approaches include fission track length distributions and $^4\text{He}/^3\text{He}$ diffusion experiments combined with (U–Th)/He dating.

Thermochronological Record of Valley Incision

Low-temperature thermochronologic studies of major river gorges in Eastern Tibet and the western Andes have been used to interpret the timing and rates of rapid fluvial incision on the flanks of large orogenic plateaux and, by inference, the timing and rates of plateau uplift. Kirby et al. (2002) used multiple thermochronometers to model the cooling histories of samples near the edge and in the interior of the Tibetan plateau. They noted that samples near the southeast margin of the plateau experienced rapid cooling from roughly 200 °C to less than ~ 70 °C in the late Miocene (~ 5 –12 Ma), whereas interior samples showed older ages for a given thermochronometer and more gradual cooling histories. To the south of the Kirby et al. (2002) study area, Clark et al. (2005) compared apatite He ages to their depths in fluvial valleys below the local plateau surface. The resulting composite age-elevation relationship show a break in slope in the late Miocene (9–13 Ma) consistent with rapid incision by rivers throughout the region. Indeed, age-elevation profiles, i.e., sets of thermochronological ages collected from different elevations within a spatially restricted domain, have been widely used to infer exhumation histories of specific areas (e.g., Wagner and Reimer 1972; Fitzgerald et al. 1995). A third spectacular example comes from the western flanks of the planet's second largest subaerial orogenic plateau (the Altiplano-Puna) in the Peruvian Andes. There, Schildgen et al. (2009) determined apatite He ages collected along strike of a major river canyon and interpreted the results as evidence for onset of ~ 2.4 km of rapid incision beginning at ~ 9 Ma (Fig. 1).

The lowest-temperature thermochronometer in wide use is apatite (U–Th)/He, which has a closure temperature of ~ 70 °C. Consequently, unique (U–Th)/He constraints on the timing of an erosional event require that the episode be of sufficient magnitude (at least 2,300–3,500 m of denudation in areas with geothermal gradients of 20–30 °C/km) such that apatite ages from rocks in a vertical transect can reveal the timing of unroofing. New and still developing techniques such as $^4\text{He}/^3\text{He}$ (Shuster and Farley 2003) and optically stimulated luminescence (OSL; Herman et al. 2010) thermochronometers provide the potential to constrain even lower magnitude denudational events. An illustration of the power of these new techniques comes from samples collected in alpine landscapes in mountain ranges that have been affected by glacial erosion. Apatite $^4\text{He}/^3\text{He}$ step heating results from samples in the 2-km deep, glacially carved, Rhône Valley in Switzerland show that this valley deepened by about 1–1.5 km over the past one million years (Valla et al. 2011). Results record an approximately twofold increase in local topographic relief at around

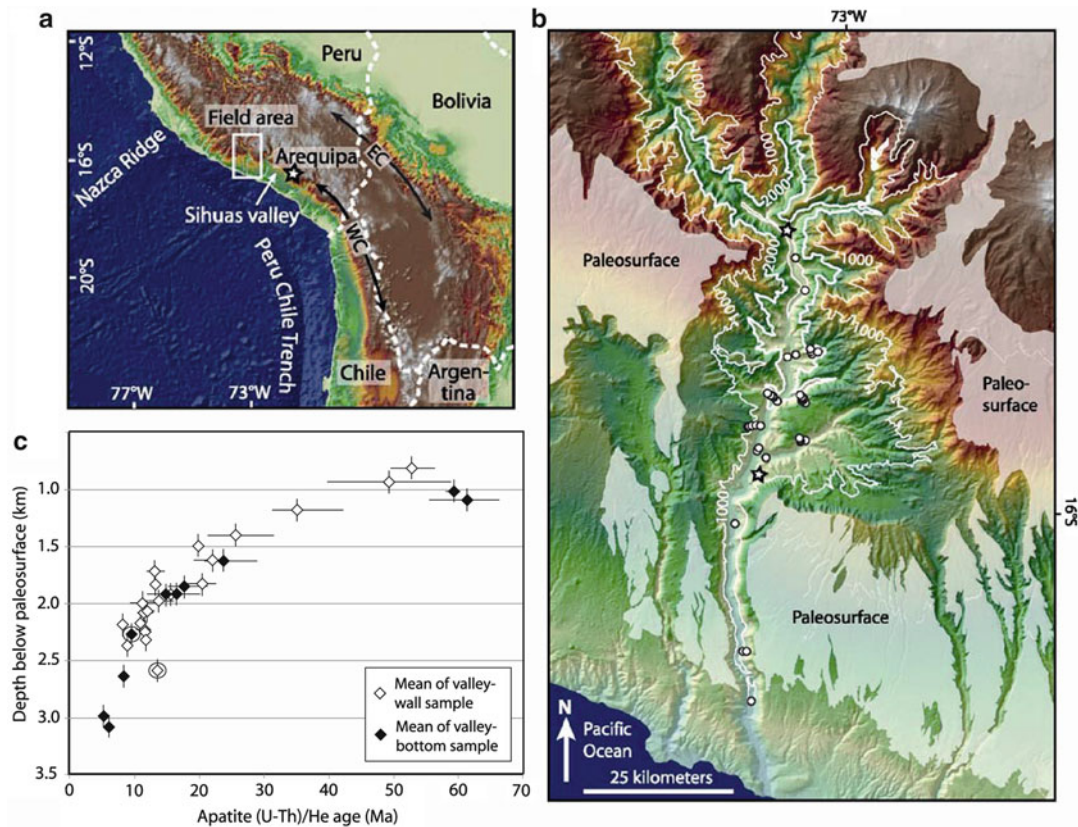


Fig. 1 (a, b) Location maps showing Ocoña canyon in southwest Peru and thermochronologic sample sites for apatite (U–Th)/He dating. Topography in (b) is illustrated by a 30 m resolution semitransparent DEM colored by elevation draped over a hillshade layer. *White shading* indicates the relict surface over which a spline surface was fit to determine surface topography prior to surface uplift and incision. Depths of samples below the paleosurface are indicated by 1,000 m contour lines. (c) Apatite (U–Th)/He data plotted against depth beneath reconstructed paleosurface (Data and illustration modified from Schildgen et al. (2009))

one million years ago and imply that the onset of intense glaciations and rapid valley incision within the European Alps correlates with the global mid-Pleistocene climatic transition from symmetric 41,000 year to strongly asymmetric 100,000 year glacial/interglacial oscillations. Valla et al. (2011) further proposed that this major climatic change may have enhanced glacial conditions by permitting larger, more erosive, and longer-lived alpine glaciers to develop. As a result, valleys could be lowered by glacial incision while still preserving high-elevation landscape elements.

Reconstruction of Paleotopography Using Topographic Bending of Isotherms

Topographic effects on thermochronological age-elevation profiles result from the fact that near-surface isotherms are not horizontal but are deflected by the topography (Fig. 2). The intensity of this perturbation and its depth of penetration are governed by the amplitude and wavelength of the topography (Braun 2002a). Different approaches used to exploit the topographic deflection of isotherms in order to derive quantitative and independent estimates of both denudation and relief histories are presented in the three following sections.

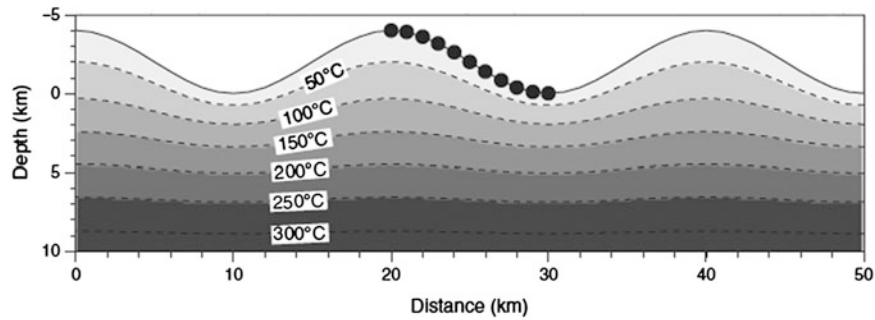


Fig. 2 Synthetic model simulating the upper-crustal thermal structure for a steady-state sinusoidal topography with wavelength $\lambda = 20$ km, amplitude $A = 4$ km and a constant 1 km/Myr denudation rate. *Black circles* denote synthetic samples collected along an elevation profile (Figure from Van der Beek et al. 2010)

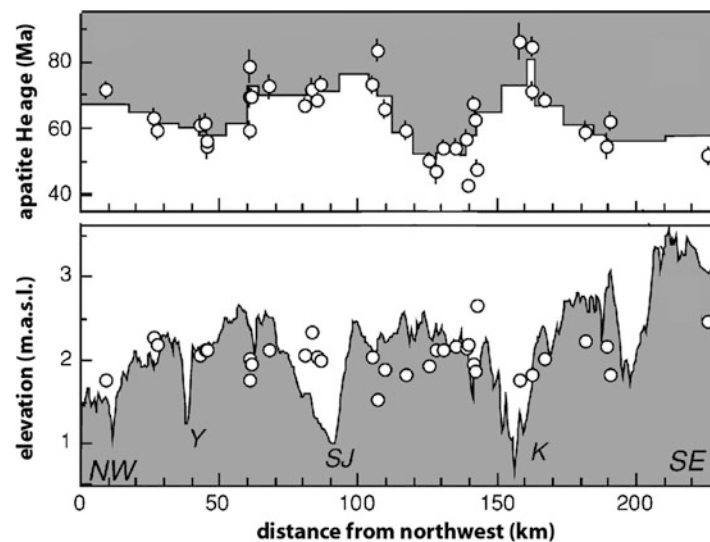


Fig. 3 Plots of elevation (*lower*) and apatite He age (*upper*) for samples from a north-to-south transect along the western Sierra Nevada Range, California. Samples collected near major valleys have older ages than samples collected at the same elevation but farther from valleys. Major features include the Yosemite (Y), San Joaquin (SJ), and Kings (K) canyons. The *upper* panel shows the Along with individual apatite (U–Th)/He ages, and the *upper* panel also shows a running average age (*stepped curve*). The data suggest that samples collected near major canyons passed through their closure isotherms earlier than samples away from the canyons because of the downward warping of isotherms beneath wide valleys (Adapted from House et al. 1998)

The House et al. (1998, 2001) Sierra Nevada Studies

One of the earliest, if not the first, application of these principles to detecting paleotopography was the work of House et al. (1998, 2001) in the Sierra Nevada of California. House et al. showed that samples collected at about the same elevation along the Sierra Nevada Range had very different apatite (U–Th)/He ages, depending on their proximity to major valleys such as the Yosemite and San Joaquin canyons. As shown in Fig. 3, samples near canyons had much older ages. The simplest explanation for those results is that as samples were exhumed, they passed through their closure temperatures at depths that depended on the overlying topography, as suggested in Fig. 2. If true, the major range-traversing canyons seen today must have been present in roughly the same positions between 60 and 80 million year ago.

Spectral Approaches

Because the interpretation of low-temperature thermochronological age data is difficult and relies on the knowledge of local parameters that are usually poorly constrained, notably, the geothermal gradient (House et al. 1998, 2001), Braun (2002b) developed a new methodology, called the “spectral method,” to interpret thermochronometric data that does not suffer from this drawback. Spatial variations in erosion rate that result in changes in topographic relief will therefore be preserved in age-elevation relationships. Specifically, age-elevation relationships over different topographic wavelengths contain information about relief change at various scales, as well as the mean erosion rate over the whole landscape. In general, the spectral approach is most sensitive to the most-recent relief changes and those that occur over the longest topographic wavelength. The spectral method requires several important assumptions including a steady and uniform (except as perturbed by topography) geothermal gradient, stationary landforms that may grow or shrink over time, and no horizontal advection of rock (which would result in a phase shift of the gain function) (Braun 2002b). Most importantly, because this approach implicitly associates age variations over long wavelengths with transient topography, it requires uniform rock uplift rates throughout the domain used in the analysis. If active structures or isostatic rebound partition uplift over the landscape domain, age variations over long wavelengths may reflect erosion rate variations that are not associated with relief change. Young cooling ages in the core of a mountain range, relative to the flanks, for example, may not necessarily be caused by decreasing relief of the range. Instead, those younger ages may reflect high rates of rock uplift in the core due to focused crustal strain or isostatic rebound of a deep crustal root.

Numerical Models and Inversion of Thermochronological Ages

Important assumptions required by the House Sierra Nevada studies and spectral methods have led to a major challenge: can we describe or predict the temperature structure in the Earth’s upper crust with sufficient accuracy to infer exhumation rates from cooling rates? This challenge is further complicated when one realizes that the process of exhumation itself perturbs the temperature structure, as does the finite amplitude topography that we wish to measure or date. Other challenges inherent to any modeling exercise that attempts to reproduce data include incorporation of available knowledge of the physical and geological processes (i.e., faulting, sedimentation, magmatism, fluid circulation) that can affect the thermochronological age during cooling of the rock sample, as well as uncertainties contributing to noise in the data. Consequently, sophisticated 3D numerical methods have been developed to quantify landscape evolution from thermochronological data. Braun et al. (2012) developed a numerical model, called PECUBE, designed to predict the 3D thermal structure of the crust in regions subject to complex exhumation and landform evolution histories (Fig. 4). The model is coupled with an age-prediction model that produces synthetic thermochronologic ages. Predicted ages can be compared to data from samples collected in the region.

Recent studies (e.g., Braun and Robert 2005; Herman et al. 2007) have combined PECUBE with an inversion scheme based on the neighborhood algorithm to search the parameter space and extract best-fitting scenarios for denudation and relief histories from the data (Braun et al. 2012). Glotzbach et al. published a nice example of inversion of a thermochronological dataset collected along the Mont Blanc tunnel, crossing the Mont Blanc external crystalline massif in the Western Alps (Glotzbach et al. 2011). Inverse PECUBE modeling was used to better quantify the Neogene exhumation and relief history of the Mont Blanc Massif. Results of the inversion shown in Fig. 5 suggest that the most probable scenarios are characterized by an approximate doubling in relief

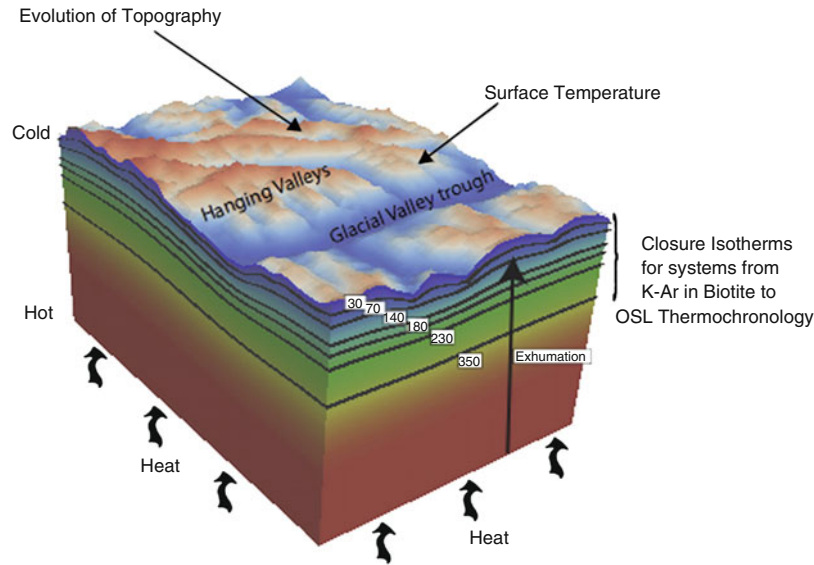


Fig. 4 Basic philosophy of the PECUBE model. Shown is a crustal block, subjected to a uniform uplift rate and assuming a time-varying, finite amplitude surface topography. The sides of the block show the thermal structure (note the compression of isotherms near the surface as a result of rapid rock advection). In *black* are shown the isotherms corresponding to various thermochronometers (Figure from Braun et al. (2012))

starting at 0.9 ± 0.8 Ma and a consequent increase in local (but not regional) exhumation rate at the same time (Fig. 5a, b).

Tracer Thermochronological Approaches

As presented above, thermochronological ages can be used to quantify landscape evolution over long time scales ($>10^6$ years) and thus tend to represent regional-scale erosion rates given that geomorphic processes tend to migrate spatially on shorter time scales. Dating of detrital minerals in the sediment load of river drainages provides an alternative for examining erosion processes. The tracer thermochronology method uses detrital cooling ages as a tracer, which links modern stream sediment to upstream bedrock sources. For example, Vermeesch (2007) used cooling ages to constrain the source of alluvial boulders to upstream bedrock sources. At the drainage scale, Stock et al. (2006) used a tracer method to argue for above-average erosion rates in the upper reaches of a drainage because of the abundance of old cooling ages in the fluvial sediment. McPhillips and Brandon (2010) established a statistical basis for the tracer thermochronology approach and used this approach to examine relief change in two major Sierra Nevada drainages: the Kings and the San Joaquin. The detrital cooling ages from the Kings River drainage show an excess of young ages relative to what would be expected from uniform erosion, whereas the San Joaquin River drainage shows an excess of old ages. These thermochronology results were interpreted to indicate increasing relief in the Kings drainage. The results from the San Joaquin drainage were more difficult to interpret, but were ultimately interpreted to indicate steady or declining relief in the basin.

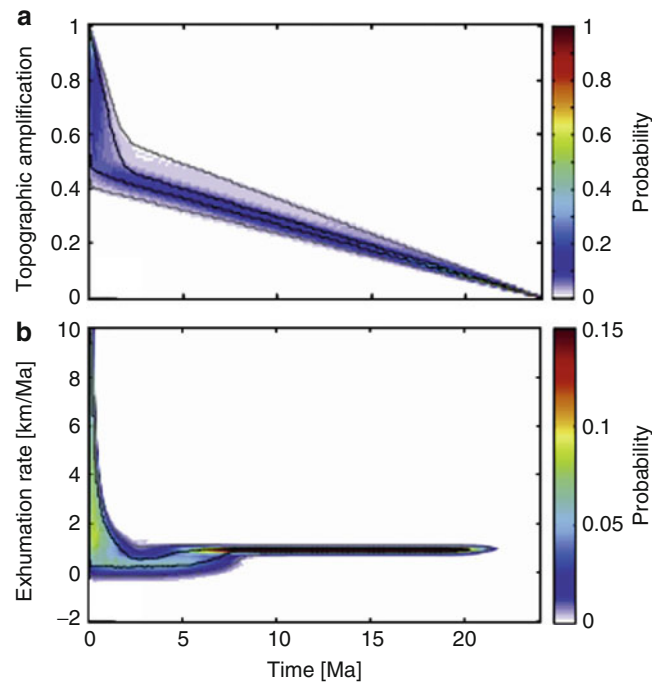


Fig. 5 Exhumation and relief evolution path of the Mont Blanc massif. Probabilities and corresponding 2σ (*gray*) and 1σ (*black*) confidence intervals are constructed using re-sampling of the dataset. **(a)** Most probable relief evolution and **(b)** total exhumation history (i.e., including both regional exhumation and local valley carving) for a valley sample. A value of 0 of the relief amplification factor implies a flat paleosurface at the present-day highest elevation and 1 implies paleo-relief equal to the present-day relief (Modified from Glotzbach et al. (2011))

Summary

Spatial patterns of ages that correspond to cooling through low-temperature characteristic of the shallow crust can be used to infer paleotopography in several ways. Multiple thermochronometers or age-elevation profiles collected along areas of large topographic relief, such as valleys incised into orogenic platforms like the Tibetan and the Andean plateaux, can be used to date their incision ages (Kirby et al. 2002; Clark et al. 2005; Schildgen et al. 2009). The recent development and application of lower-temperature thermochronometers such as $^4\text{He}/^3\text{He}$ (Shuster and Farley 2003) and OSL (Herman et al. 2010) techniques provide the potential to constrain lower magnitude denudational events, such as the incision of glacial valleys (Shuster et al. 2011; Valla et al. 2011). The antiquity and amplitude of long-wavelength topographic development can be estimated by dating samples collected across the landform at similar elevations and then exploiting superimposed short-wavelength topography, as in the House et al. (1998, 2001) studies. Sophisticated 3D numerical models that simulate the thermal structure of the Earth can be used to invert thermochronological data and separately quantify rock uplift and relief histories (see Braun et al. 2012, for a recent review of this approach). Finally, thermochronological ages can also be used as tracers in modern fluvial sediments to repartition areas of greater or lesser erosion in a catchment (Stock et al. 2006; Vermeesch 2007; McPhillips and Brandon 2010).

As with any analytical technique, the application of thermochronology for understanding landscape evolution must overcome distinctive challenges that can complicate interpretations. Indeed, quantifying paleotopography requires important assumptions, not the least of which is that the thermal field in the shallow crust is affected mostly by topography and not by variations in advection

by fluids, heat production, arc magmatism, or other factors. Another important assumption for most approaches involving spatial variations of surficial bedrock cooling ages is that rock uplift beneath a landscape is uniform, a postulation that is most likely met over short wavelengths in tectonically inactive settings.

Cross-References

- ▶ [⁴He/³He Dating](#)
- ▶ [Apatite](#)
- ▶ [Exhumation \(Thermochronology\)](#)
- ▶ [Fission Track Dating](#)
- ▶ [Tectonic Processes \(Thermochronology\)](#)
- ▶ [Thermochronology, Detrital Zircon](#)
- ▶ [\(U–Th/He\) Dating](#)

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Biostratigraphy

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Introduction

Biostratigraphy (from Gr. *bios*, life; L. *stratum*, bed; Gr. *grapho*, write (Brown 1991)) is arguably one of the most broadly used stratigraphic methods in Earth Sciences and concurrently one of the most misrepresented/misunderstood disciplines. In a strict sense, biostratigraphy is the *objective* subdivision of the stratigraphic record based on its paleontological content for the purpose of relative dating and correlation, and, as such, it is described in international stratigraphic guides and national codes. In the broadest sense, biostratigraphy encompasses the whole spectrum of disciplines that reconstruct various facets of Earth history from its sedimentary record, for academic and industrial purposes. In this view, biostratigraphy is central to the reconstructions of paleoceanographic and paleoclimatic history, the formulation of evolutionary theories, the description of sedimentary architecture and of sea level history, and, foremost, the discovery of geological time (or geochronology). This has been emphatically demonstrated by McGowran (2005) who illustrated the unprecedented role of microfossil biostratigraphy in the discovery of Earth history.

In this entry, biostratigraphy is discussed as a method, and I define its components and discuss the biostratigraphic correlations. This leads to the problem of diachrony and the importance of biostratigraphy in determining the occurrence of stratigraphic gaps in sedimentary sections. Finally I examine the significance of integrated biostratigraphy to soundly interpret stratigraphic successions and discuss a few examples of its role as a means to *interpret* the paleontologic record. The vertical succession of strata constitutes a clear evidence of the passage of geological time, as Steno (1669) discovered, leading to the formulation of the three principles that would become the cornerstone of Earth Sciences. But what are the relations of strata to time? Is there a one-to-one relationship between rock and time, so that any stratigraphic interval (thickness, measured in meters [m]) can be readily converted into an equivalent amount of time (duration (for distinction between Ma and Myr, the reader is referred to Aubry (2009)), measured in million years [Myr]), and any stratigraphic level (positioned with reference to Meter 0) converted into a geological date (positioned as a point expressed as mega-annum [Ma])? Or is the stratigraphic record discontinuous, with concealed unconformities that complicate the extraction of information about time from stratal successions?

Biostratigraphy and Paleontology

Biostratigraphy is intimately related to paleontology. This is because biostratigraphy involves mostly the study of *extinct species*, and for this reason, it was first known as *paléontologie stratigraphique* (stratigraphic paleontology) (D'Orbigny, 1852).

Species have a *life span*, which is the collective life span of all the specimens in it, from the moment when the species evolved to the moment when it became extinct. Most of the species that

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ever lived are now extinct, but many are known from their fossils, which are named based on the Linnaean nomenclature of genus and species names just as any living species. Not all fossils are of skeletonized organisms, but the majority are, which results in biostratigraphy being only compulsory for the relative dating and correlation of the Phanerozoic sedimentary strata. Its usefulness extends, however, to the strata just below the Cambrian, assigned to the Vendian series, in which soft-body animals and traces of their activities (burrows in particular) are common and diverse.

The vertical extent over which a species occurs in sedimentary rocks is called its *range*, which is representative of the life span of that species in the area where its fossils are found. The range is delineated between two stratigraphic horizons (Fig. 1). A species (e.g., species D in Fig. 1) is absent below the lower (and older) stratigraphic horizon but is present above it. It is also absent above the upper horizon but is present below it. Stratigraphers refer to the presence of a taxon at a stratigraphic level as *occurrence* (the meaning of “occurrence” seems to have changed through time. The Roget’s II, 1980 (p. 645), gives three definitions for occurrence: (1) “something that happens” [= circumstance]; (2) “something significant that happens” [=event]; and (3) “the condition or fact of being present” [= presence]. In contrast, the Roget’s II 2014 (<http://thesaurus.com/Roget-alpha-index.html>) gives two definitions of occurrence: (1) “the action, fact, or instance of occurring” and (2) “something that happens: event, incident”. I stress here that “stratigraphic occurrence” should be understood as “stratigraphic presence”). Thus, the lower (older) horizon contains the *lowest occurrence (LO)* of the taxon, which is the *oldest stratigraphic level in a section* where the species is present, while the upper (younger) horizon contains the *highest occurrence (HO)*, which is the *youngest stratigraphic level in the same section* where the species is present. LOs and HOs are *biohorizons*. The LO of a macrofossil such as an ammonite species may appear significant enough to qualify as a biohorizon, whereas the LO of a 5 µm coccolith may seem rather insignificant. Yet, the same principle applies to microfossil (~63–250 µm) and nannofossil (<63 µm to 2 µm) taxa as to macrofossils. LOs and HOs are stratigraphic terms, positioned in a section with respect to a specific point of reference.

Fossils were first treated as unrelated objects, as buttons are, for instance, some sharing similar ranges, whereas others would not. The concept of *faunal succession* (Smith, 1815) was derived from this basic observation and prior to the acknowledgement of the evolution of organisms. But fossils are related to one another through organic evolution, which explains their enormous morphologic diversity and the organization of this diversity in specific stratigraphic intervals marked by the success of particular groups or clades (thus the “Age of Fishes,” those “of Reptiles,” “of Dinosaurs,” and “of Mammals”) and the arrow of time that is perceived through the unfolding of this diversity. The arrow of time confers upon biostratigraphy its uniqueness: it is the only *non-iterative method* of relative dating and the counterpart of the radioisotopic methods in numerical dating. Biostratigraphy is the only means of relative dating that is self-sufficient, although its integration with other stratigraphic means (magnetostratigraphy, isotope stratigraphy, sequence stratigraphy) enhances its potentialities.

The ideal species in biostratigraphy are those with abundant and widespread geographic occurrences during their life, regardless of latitudes and depth of deposition (Table 1). They are marine planktonic species, among which are the Paleozoic graptolites (up to several mm long,

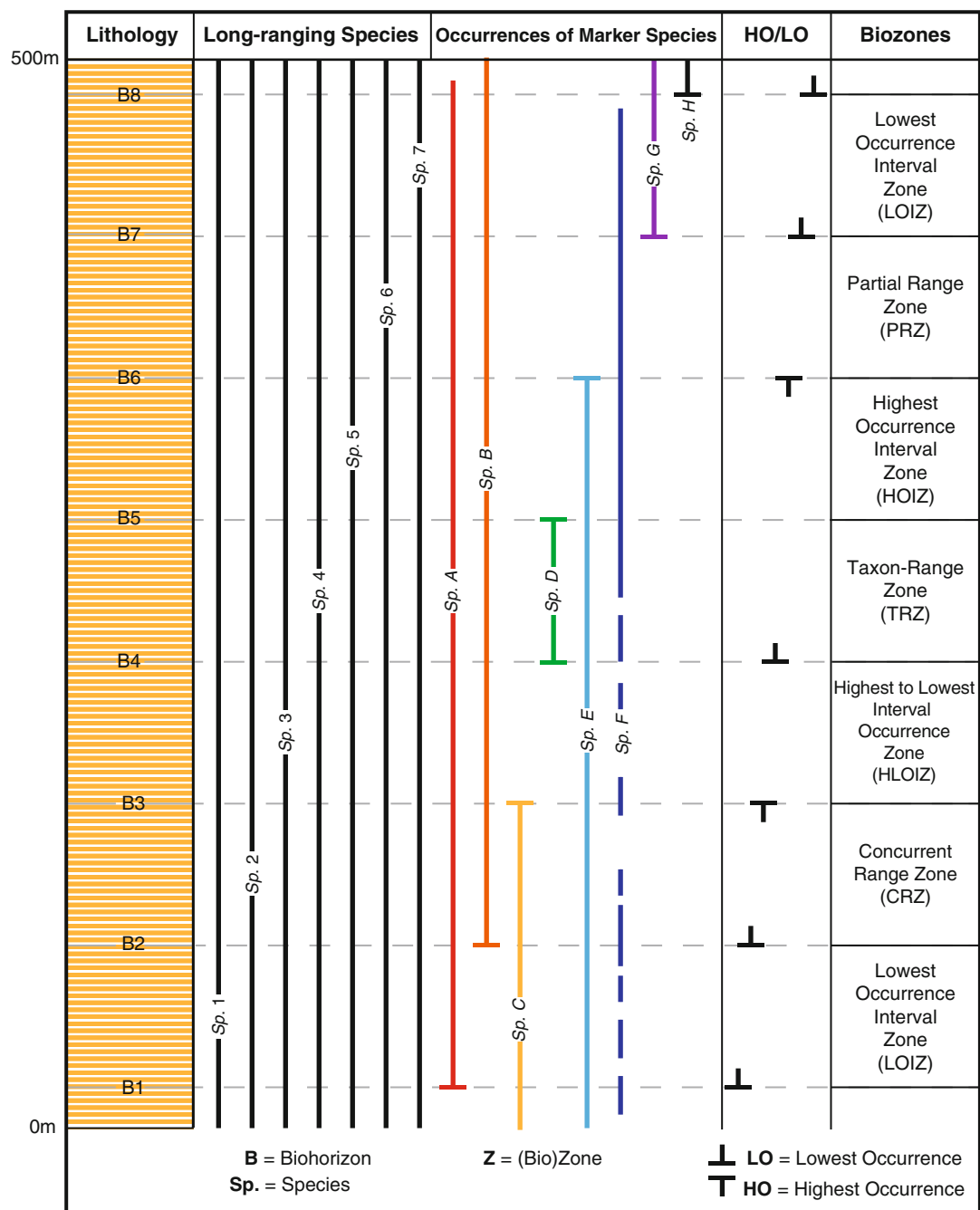


Fig. 1 An example of biostratigraphic subdivision of a section based on the range of selected species. Biostratigraphic subdivision is arbitrary in the sense that a few species are selected among many to construct a biozonal framework. In this example, the HO of *Sp. F* may have been chosen rather than the LO of *Sp. H* to delineate biohorizon B8

Hemichordata), the phosphatic conodont elements (~200 µm to 5 mm; Chordata), the Paleozoic and Mesozoic cephalopods (Mollusca), and the minute Mesozoic and Cenozoic planktonic protists that belong to unrelated clades but are preserved together in deep-sea sediments and among which the

Table 1 Main taxonomic groups involved in biostratigraphy. Biostratigraphy relies on eukaryotic organisms, those that have evolved a diversity of skeletal morphologies, and these comprise protists, invertebrates and vertebrates animals, and (mostly) vascular plants. It can be readily inferred from this that not all fossils have equal potential with regard to biostratigraphic usefulness. Species that, alive, had a narrow geographic distribution, as most benthic species did, do not constitute good stratigraphic markers, at least not over long distances. (The term biomarker does not designate stratigraphic markers but chemical molecules characteristic of specific organisms.) Benthic invertebrates, such as bivalves and echinoderms, are biostratigraphically useful, but only regionally. This is true also of benthic protists such as large benthic foraminifera (e.g., the Paleozoic fusulinids, Mesozoic *Orbitoides*, Cenozoic *Nummulites*) of warm water epicontinental deposits and of green algae such as charophytes in brackish and lacustrine deposits. The distribution of vertebrates and vascular plants is also limited by climatic barriers. Fossilized parts (shells, tests, gyrogonites, teeth, leaves) of these organisms usually serve for regional biostratigraphic subdivision, but their trace fossils (burrows, foot tracks) may occasionally be helpful as well (Olsen et al., 2002)

Biological group	Lifestyle	Phyla/groups	Biostratigraphic applications
Invertebrate animals	Benthic	Brachiopoda	Regional
		Echinodermata	
		Mollusca	
	Planktonic	Hemichordata (graptolites)	Broad
Vertebrate animals	Terrestrial		Regional
	Marine	Chordata (conodonts)	Global
Nonvascular plants	Brackish lacustrine	Charophyta	Regional
Vascular plants	Terrestrial		Regional
Unicellular organisms (“protists”)	Marine, benthic	Large benthic foraminifera	Regional
	Marine, planktonic	Coccolithophores	Global
		Diatoms	High latitudes
		Dinoflagellates	Epicontinental
		Foraminifera	Global
		Radiolarians	Low latitudes

planktonic foraminifera and coccolithophores occupy a prominent role. Both are abundant in deep-sea oozes and chinks, and they also occur in epicontinental deposits; additionally, coccoliths constitute the fine fraction of many such deposits. Examples in the following discussion are borrowed from these two groups, because they have contributed more to biostratigraphic thinking than any other group, but the same principles and concepts in biostratigraphy apply to all paleontological groups.

Basic Concepts in Biostratigraphy

The use in any form of fossils for relative dating and correlation is part of biostratigraphy. For instance, morphologic trends in a genus or differences in optical properties among closely related species may be used to characterize specific chronostratigraphic intervals (Figs. 2 and 3). These methods result, however, in broad age assignments. Greater resolution is achieved with the

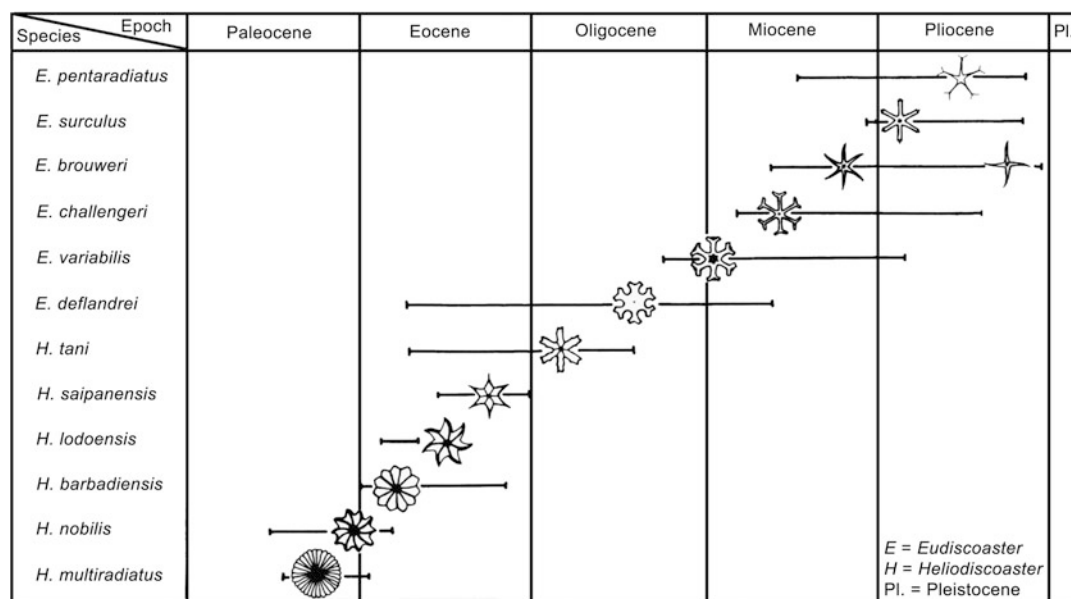


Fig. 2 Morphologic trends in coccoliths (here discoasters) and relative age assignment. Each morphologic group is symbolized by a species (*left*) (Modified after Martini, 1971b, Fig. 39.1). Occasionally, when preservation in a stratigraphic section is poor, there are no other means than broad morphology to determine its relative age. Also anomalous mixture of morphologies (e.g., morphologies represented by *E. surculus* and *H. multiradiatus*) is indicative of reworking (or contamination, depending on circumstances)

subdivision of stratigraphic succession into biostratigraphic zones (Figs. 1 and 4, Tables 2 and 3) based on the stratigraphic ranges of selected species or other selected criteria. Occasionally, poor preservation of fossil assemblages hampers fine resolution, leading to the recourse of less satisfactory methods (Figs. 2 and 3).

Biozone

Concept

The basic unit of biostratigraphy is the *biostratigraphic zone*, or *biozone* for short, which is a stratigraphic interval measured in terms of thickness (generally in meters and its derivatives; occasionally feet in the industry) and characterized by selected aspects of its fossil content. A biozone is delineated between two biostratigraphic surfaces (biohorizons) that determine its *base* and *top*. Most horizons are the LOs and HOs of chosen taxa (see above). However, other biohorizons may be used, such as a surface across which the abundance of a species considerably increases or across which a taxon is seen to have arisen from an ancestral species. Superposed biozones are separated by *zonal boundaries* so that the top of the underlying zone is also the bottom of the overlying zone. A sequence of biozones based on the same paleontological group is referred to as a *biozonation* or *biozonal scheme*.

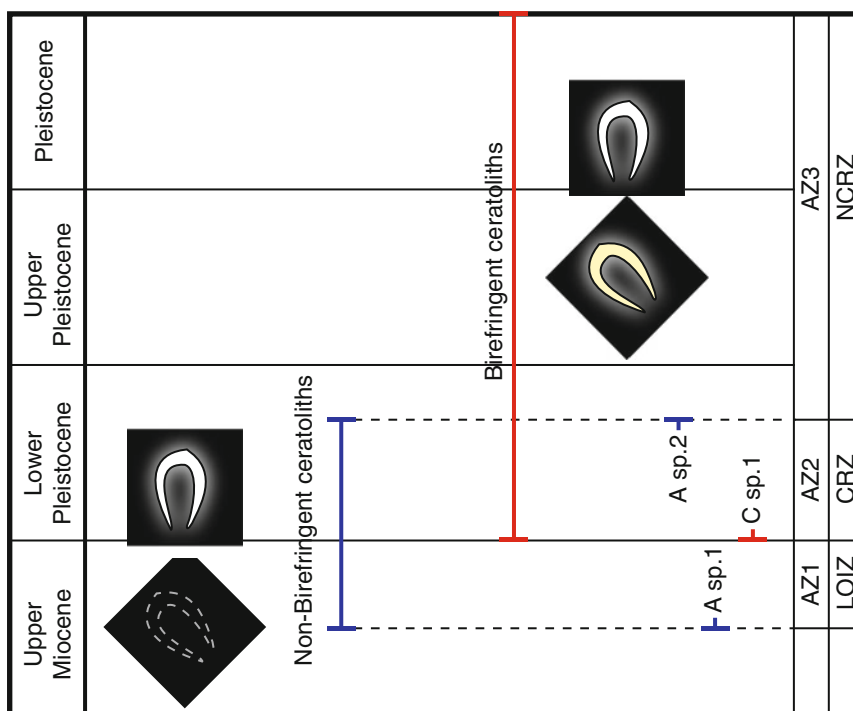


Fig. 3 The use of the optical properties of some coccoliths (here ceratoliths) helps delineate three biostratigraphic intervals that are correlatable to chronostratigraphic units. This may be useful when coccolith assemblages have been strongly affected by dissolution. The three biostratigraphic intervals can be regarded as assemblage zones, the older one comprising only species of non-birefringent ceratoliths (genus *Amaurolithus*) and only them; the younger zone comprising only species of birefringent ceratoliths (genus *Ceratolithus*) and only them; and the intermediate zone comprising species of both birefringent and non-birefringent ceratoliths. Note that the lower two intervals could also be described in succession as follows: (1) lowest occurrence interval zone (between the LO of the oldest species of *Amaurolithus* [A. sp. 1] and the LO of the oldest species of *Ceratolithus* [C. sp. 1]) and (2) concurrent-range zone (from the LO of C. sp. 1 to the HO of the last representative of the genus *Amaurolithus* [A. sp. 2])

Types of Biozones

Biozones differ from one another in two aspects. One is the means used for defining boundaries, in which the base and the top of a zone may be characterized by LO(s) and HO(s) of a taxon (or taxa). The other is the content of the zone itself, including occurrence and abundance of one or several taxa. The combination of both characters results in ten types of biozones distributed in two categories (interval and range zones, Fig. 4). In assemblage and abundance zones, the emphasis is placed on the content of the zone. In lineage and interval zones, the emphasis is placed on the boundaries, whereas in concurrent-range, Oppel, and taxon-range zones, it is placed on both content and boundaries. The number of taxa involved in the definition of biozones varies from a single one (abundance and taxon-

range zones) to several (assemblage and Oppel zones). Three species are involved in the definition of a lineage zone (or phylozone) and a partial range zone. A minimum of two species is needed for defining concurrent-range and interval zones. Each type of zone has strengths and weaknesses (see below), and it is important to know the type of zone used for biozonal assignment in order to evaluate its reliability.

Biozones are (or should be) established based on morphologically characteristic species whose LOs and HOs can be consistently delineated in sections over broad geographic areas. They may be subdivided into *subzones* and regrouped into *superzones* (Fig. 5). A biozone is subdivided into subzones when species involved in the subzonal definition have inconsistent occurrences, for instance, exhibiting consistent LO, HO, or both in some sections although not present in others. Superzones are introduced when the older and the younger boundary of the oldest and youngest biozones, respectively, are particularly prominent (easily identified and geographically consistent).

Naming a Biozone

Biozones (and super- and subzones) are *formally defined and named* stratigraphic units. The procedures for their establishment are explained in the *International Stratigraphic Guide* and do not need repetition here. However, it is important to emphasize that the naming implies that each biozone is unique and should be used as defined. Its designation includes the type of zone that is being defined and the name(s) of the species that serves for its definition. The (Miocene) *Eudiscoaster quinquerramus* Taxon-Range Zone (Martini, 1971a), the (lower Eocene) *Pseudohastigerina wilcoxensis*/*Morozovella velascoensis* Concurrent-Range Zone (Berggren and Pearson, 2005), and the (Cambrian) *Trichophycus pedum* Assemblage Zone (Landing et al., 2013) may serve as examples.

Long taxonomic names in Latin do not, however, ease communication among scientists other than specialists of the groups whose species are involved in zonal definitions. Thus, the most commonly used biozonations are codified with acronyms representing the interval, taxonomic group, and/or geographic area concerned by a specific zonal scheme, associated with a number corresponding to the position of the zone in the numerical succession of zones as counted in stratigraphic succession (Table 4). The Zone NP1 to Zone NP21 and Zone NN1 to Zone NN21 of Martini (1971a) and the Zone P1 to Zone P4, Zone E1 to Zone E16, and Zone O1 to Zone O6 of Berggren and Pearson (2005) are among the most commonly used in deep-sea stratigraphy. Examples of biozonations are given in Figs. 6 and 7.

Biostratigraphic zones are equivalent, in their own category, to lithostratigraphic and chronostratigraphic units, but they are not as strictly established. Whereas the latter require stratotypes, citations of reference section are only encouraged for biostratigraphic zones. Composite reference sections are generally necessary for zonations that cover a large chronostratigraphic interval. In contrast, it is highly recommended that the taxa used in zonal definitions be described as clearly as possible and illustrated (see below).

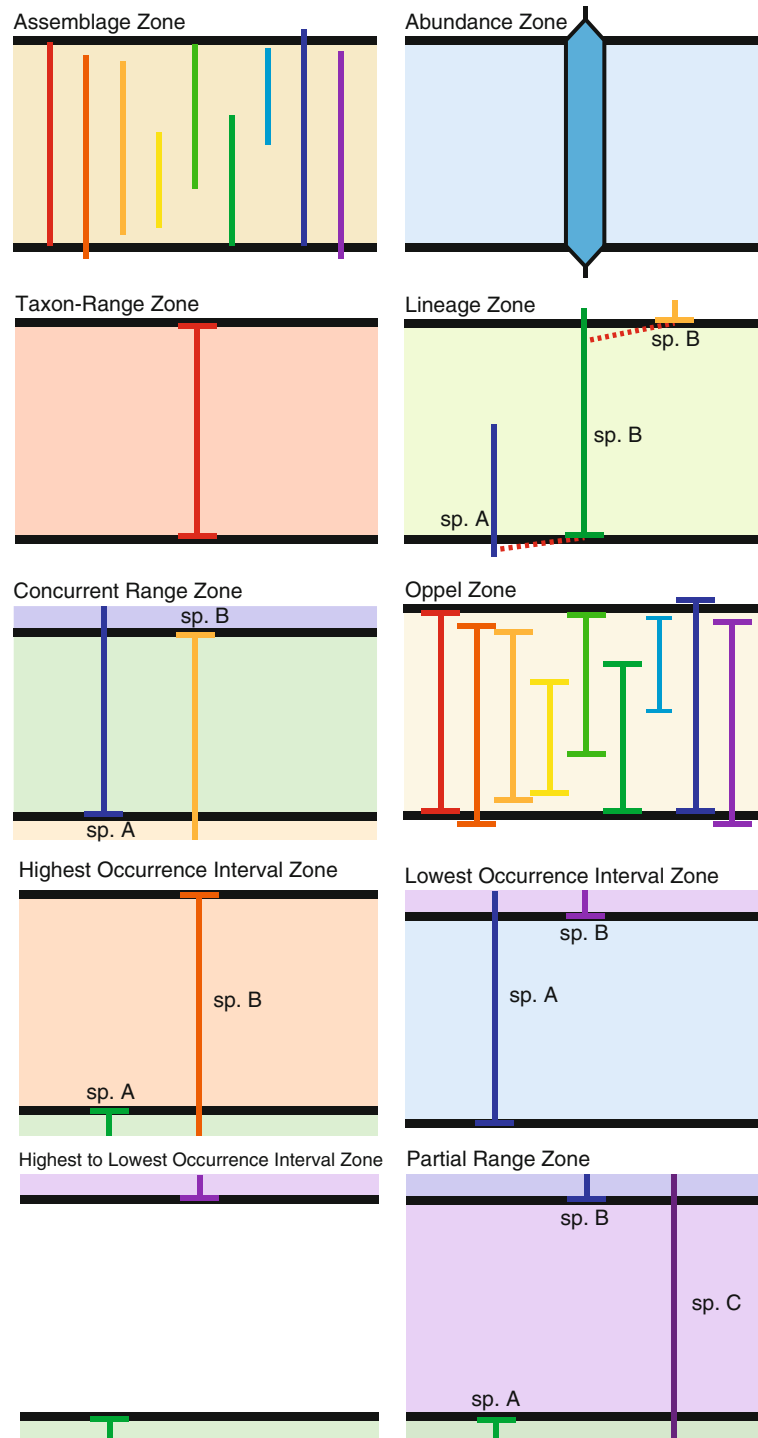


Fig. 4 Types of biostratigraphic zones. An assemblage zone (AZ) is a stratigraphic interval characterized by the co-occurrence of several taxa in combinations that may vary laterally and vertically. The taxa may be long ranging, with only one or two having its LO or HO in the zone. AZs are mostly defined in shallow water or land deposits on macrofossils. An abundance zone (AZ) is a stratigraphic interval characterized by the notable abundance of a specific taxon. The placement of the zonal boundaries may be a matter of discussion, and the percentage of a taxon in the zone may vary broadly, depending on its usual frequency. A taxon-range zone (TRZ) is defined by the total range of a taxon. A lineage zone (LZ) is defined between two horizons that record the evolutionary transition of the species from its ancestor (base of the zone) to its descendent (top of the zone). TRZ and LZ are similar in being characterized by a single taxon, but differ fundamentally in the nature of their boundaries. A concurrent-range zone (CRZ) is the interval defined

Biohorizons

Just as a stratigraphic horizon is “an interface indicative of particular position in a stratigraphic sequence” (Hedberg 1976, p. 14), a biohorizon is a “surface, or interface across which there is a significant and distinctive change in biostratigraphic characters” (Salvador, Ed., 1994, p. 56). The LO and HO of each species are potential biohorizons. However, only a few such stratigraphic occurrences achieve the status of useful biohorizon. There are many reasons for this. To qualify, species must be common where they occur, their morphology must remain sufficiently stable under different environmental conditions for the species to be identifiable in different settings, and their stratigraphic range with respect to broadly co-occurring taxa must be consistent. Thus, the most prominent biohorizons serve as zonal boundaries. However, as stratigraphic investigation continues and as attention is given to specific taxonomic entities, new biohorizons are delineated, which increases the biostratigraphic resolution within zones and subzones. Biohorizons may be the LOs and HOs of additional species, but also any prominent morphologic change (in size, shape, or ornamentation) or abundance change (of a species or in diversity; or between two taxa, the abundance of one species increasing while that of the other decreasing [the crossover biohorizon in nannofossil stratigraphy]) are recorded over long distances.

Biostratigraphic Correlations

The method of *biostratigraphic correlation* consists in recognizing in lateral sections biohorizons that have been formally defined in a reference section and to draw lines of correlation between them on this basis. In this manner, biozones are extended laterally to locations as far as the biohorizons can be identified. Beyond the furthest locations, the biozonation is no longer applicable. In practice, however, it is one thing to define a biozonal scheme based on well-preserved fossils of species in an extended section and another to recognize the same zonal scheme in sections elsewhere. When the species have been soundly selected and preservation is as good in the lateral sections as in the reference section, the characterization of the biozones and delineation of their boundaries are made with high confidence. However, this is not always the case, and difficulty may increase with increasing geographic distance and in particular across latitudes even with planktonic organisms (Fig. 7). Also each type of biozone has its own set of strengths and weaknesses that cause uncertainty in its lateral extension, recognition, and correlation (Table 5). An insufficiently recognized problem is that the possible combinations between the seven commonly used types of biozone do not number 49 as statistics would imply, but much fewer (12). The most reliable types are the taxon-range and the concurrent-range zones because they are defined by content and boundaries (see above). However, the two cannot be in immediate succession, but are necessarily separated either by a highest occurrence interval zone, a highest to lowest occurrence interval zone, or a partial range zone, which are less reliable (Figs. 8 and 9). In other words, the least dependable types of biozone



Fig. 4 (continued) between the LO of one taxon and the HO of another taxon. A CRZ is marked by the co-occurrence of two species. An Oppel zone is a hybrid between a concurrent-range and an assemblage zone in that it is comprised of several taxa (as an AZ) whose ranges are mostly restricted to the zone (unlike an AZ and unlike a CRZ which may be comprised of two long-ranging taxa but whose respective lower and upper ranges overlap). Oppel zones were mostly used in ammonite-based stratigraphy. Interval range biozones (IRZ) are those defined by the range of one taxon to the exclusion of another one and may correspond to the interval between (1) the HO of one species and the HO of another species, (2) the LO of one species and the LO of another species, and (3) the HO of a species and the LO of another species. A partial range zone (PRZ) is defined by the occurrence of a selected species between the HO of a species and the LO of another species. A PRZ is a constrained interval zone of the latter type

Table 2 Classification of biostratigraphic zones in the *International Stratigraphic Guide* (1976, 1984) and the *North American Stratigraphic Code* (2005). Note the change in position of the lineage zone, from a type of range zone in Hedberg (ed., 1976) to an independent type in Salvador (ed., 1994), the abandonment of the Oppel zone, and the agreement between the current guide and code (North American Commission on Stratigraphic Nomenclature, 2005). Although the term is not used in Hedberg (ed., 1976, p. 61), the concept of partial range zone is explicit in it, and Salvador (ed., 1994, p. 60) refers to its introduction in the report of the Stratigraphical Code Subcommittee, Geological Society of London, 1967, p. 85

Hedberg 1976		Salvador, ed., 1994		NACSN, 2005	
Assemblage zone		Assemblage zone		Assemblage biozone	
Range zone	<i>Taxon-range zone</i>	Range zone	<i>Taxon-range zone</i>	Range biozone	<i>Taxon-range biozone</i>
	<i>Concurrent-range zone</i>		<i>Concurrent-range zone</i>		<i>Concurrent-range zone</i>
	<i>Oppel zone</i>				
	<i>Lineage zone</i>		<i>Lineage zone</i>		<i>Lineage biozone</i>
Acme zone		Abundance zone		Abundance biozone	
Interval zone		Interval zone	<i>“Highest occurrence zone”</i>	Interval zone	
			<i>“Lowest occurrence zone”</i>		
			<i>“Partial range zone”</i>		

Table 3 Recent classification of biostratigraphic zones. The terms “base” and “top” for LO and HO are also used in the method of graphic correlation

Berggren and Pearson (2005) and Wade et al. (2011)	Backman et al. (2012)	This work	
Taxon-range zone	Taxon-range zone	Range zone	<i>Taxon-range zone</i>
Concurrent-range zone	Concurrent-range zone		<i>Concurrent-range zone</i>
Lowest occurrence zone	Base zone	Nonconcurrent-range zone	<i>Lowest occurrence zone</i>
Highest occurrence zone	Top zone		<i>Highest occurrence zone</i>
Partial range zone	Partial range zone	Exclusion-range zone	<i>Partial range zone</i>
			<i>Highest to lowest occurrence zone</i>
		Lineage zone	
		Abundance zone	

separate the two types upon which stratigraphic sections can be most firmly anchored to a biozonation. This places major demand on the delineation of the biohorizons that define taxon-range and concurrent-range zones (see below).

Table 4 Examples of codifications for planktonic calcareous microfossils

Code	Full name of zone	Author
N	Neogene planktonic foraminifera	Banner and Blow, 1965
P	Paleogene planktonic foraminifera	Blow, 1969; Berggren, 1969
P1 to P5	Paleocene planktonic foraminifera	Berggren and Pearson, 2005
E1-E16	Eocene planktonic foraminifera	Berggren and Pearson, 2005
O1-O5	Oligocene planktonic foraminifera	Berggren and Pearson, 2005
NP1-NN25	Nannoplankton Paleogene	Martini, 1971a
NN1-NN21	Nannoplankton Neogene	Martini, 1971b
CP1-CP19	Coccolith Paleogene	Okada and Bukry, 1980
CN1-CN19	Coccolith Neogene	Okada and Bukry, 1980
NTp1-NTp14	Nannoplankton, tertiary, Paleocene	Varol, 1989
NNTp1–NNTp	North Sea, nannoplankton, tertiary, Paleocene	Varol, 1989

Super-biozone	Biozone	Subbiozone
	Biozone 7	
	Biozone 6	
	Biozone 5	
Superzone	Biozone 4	Subbiozone 3 Subbiozone 2 Subbiozone 1
	Biozone 3	
	Biozone 2	
	Biozone 1	

Fig. 5 Superbiozones, biozones, and subbiozones. These constitute a biostratigraphic hierarchy so that the boundaries of a superbiozone are the lower and the upper boundary of, respectively, its lowermost and uppermost biozones. The division of a subbiozone necessitates the introduction of an additional stratigraphic horizon to define the subzonal boundaries, but the base and top of the lower and upper subbiozones are those of the undivided zone

Zone		Biohorizon	Epoch	
Code	Full Name			
NN2	<i>Discoaster druggi</i> Zone		Early	Miocene
NN1	<i>Triquetrorhabdulus carinatus</i> Zone			
NP 25	<i>Sphenolithus ciperoensis</i> Zone		Late	Oligocene
NP 24	<i>Sphenolithus distentus</i> Zone			
NP 23	<i>Sphenolithus predistentus</i> Zone		Early	
NP 22	<i>Helicopontosphaera reticulata</i> Zone			
NP 21	<i>Ericsonia ? subdisticha</i> Zone			
NP 19	<i>Sphenolithus pseudoradians</i> Zone			
NP 20	<i>Isthmolithus recurvus</i> Zone		Late	Eocene
NP 18	<i>Chiasmolithus oamaruensis</i> Zone			
NP 17	<i>Discoaster saipanensis</i> Zone			
NP 16	<i>Discoaster tani nodifer</i> Zone		Middle	
NP 15	<i>Chiphragmalithus alatus</i> Zone			
NP 14	<i>Discoaster sublodoensis</i> Zone			
NP 13	<i>Discoaster lodoensis</i> Zone		Early	
NP 12	<i>Marthasterites contortus</i> Zone			

Fig. 6 Examples of calcareous nannoplankton biozonation. Martini's zonation (1971a), here represented for the lower Eocene (*partim*) through Oligocene, is still in broad use. NP = nannoplankton Paleogene. The names of the zone and their code are given together with the types of biohorizons that are defined by species ranges

Aside from the latitudinal effect on correlation potentials and the uneven reliability within most biozonal schemes that is inherent to the very types of component zones, two categories of difficulties may arise in extending zonal boundaries away from the reference sections. In the first category are general difficulties that have been discussed in detail by Pearson (1998; Table 6). It can be added that the use of more than one taxon to define a zonal boundary introduces an uncertainty in its location because it is rarely the case that two species have precisely the same LOs or HOs in normal stratigraphic successions. In short, the greater the number of species involved in defining a zonal boundary, the greater the chance of characterizing it generally, but the less the precision in its delineation. This is a common problem with coccolithophore stratigraphy, for example. In the second category are difficulties relative to taxonomy.

It cannot be overemphasized that the concept of biozone is strictly dependent of the taxonomic concept(s) of the species used to define it (e.g., Hedberg, 1976, p. 55). Yet, taxonomy is a main source of uncertainty in stratigraphic correlation, and the more so that there is a general tendency to minimize this fact, in concert with the general disregard for taxonomic work in many circles today. The taxonomic problem is about consistency: (1) how to consistently recognize a species throughout its spatial and temporal range and (2) how to consistently place biohorizons so as to enhance precision in correlation.

Pearson (1998) and McGowran (2005) addressed the first question by discussing the conflict between the typological concept in paleontology and the population concept in biology. Species are not morphologically stable in the sense that no two individuals are alike, which is as obvious in fossil assemblages as it is in living populations. However, studies of living populations are mainly concerned with spatial variations, whereas studies of extinct species are concerned with both spatial *and* temporal variations. Morphologic evolution has been documented for very few protistan species (e.g., Hull and Norris, 2009; Knappertsbusch, 2000, 2007). These studies have shown complex evolutionary patterns, but with long intervals of morphologic stasis interrupted by brief intervals of high morphologic variability (in close agreement with the theory of punctuated equilibrium, see Gould and Eldredge, 1993) which lends credence to the application of the typological approach to biostratigraphy.

The second question is answered differently in the different disciplines of biostratigraphy, depending on the morphological characteristics of the fossils, as shown by the following two examples:

1. The archetypal shape in the planktonic foraminifera is a sphere, and the chambers that constitute the test are modified spheres arranged around an axis. This is the cause for an “infinite” morphologic diversity in the group and high intraspecific morphologic variability within lineages and species. Except at high rank, taxonomy in this group is dominated by morphology over structure. Specialists of foraminifera are thus confronted with a broad morphologic diversity whose significance in terms of evolutionary history must be determined. Pearson (1998) has thus advocated the use of biohorizons reflecting the evolutionary history of lineages: dispersal, extinction, pseudospeciation, and pseudoextinction biohorizons (Fig. 10).
2. Coccoliths are the articulated or loosely arranged skeletal pieces of the coccospheres of coccolithophores. Their shape varies little, but their structure differs markedly between lineages, so that taxonomy down to the genus level can be rigorously based on structure, species determinations being based on small morphological differences. The specialist here is confronted with having to determine the range of tiny fossils that may be few in the lower part of their range (possibly during species dispersal), reworked in its upper part, and whose identification is made ambiguous by poor preservation. Specialists have thus introduced semiquantitative methods

Planktonic Foraminifera											Series	Stage	
(Sub) Tropical					Transitional			(Sub) Antarctic					
Berggren, 1995				Bow (1969)	Berggren et al., 1983a, 1995			Berggren, 1992					
PL1	b	<i>Gt. cibaoensis</i> - <i>Glb. nepenthes</i> ISZ		<i>Gt. tumida</i> - <i>Glb. nepenthes</i> IZ	N	<i>Gt. puncticulata</i> IZ					Pliocene	Lower	Zancian
	a	<i>Gt. tumida</i> - <i>Gt. cibaoensis</i> IRZ			N 19	<i>Gt. sphericomiozea</i> IZ							
M14		<i>Gt. languaensis</i> - <i>Gt. tumida</i> IZ			N 17	Mt10	<i>Gt. conomiozea</i> / <i>Gt. mediterranea</i> - <i>Gt. sphericomiozea</i> IZ			AN 7	<i>Neoglobbquadrina pachyderma</i> TRZ		Messinian
M13	b	<i>Gd. extremus</i> / <i>Gt. plesiotumida</i> - <i>Gt. languaensis</i> ISZ				N 16	Mt9	<i>P. mayeri</i> - <i>Gt. conomiozea</i> IZ					
	a	<i>N. acostaensis</i> - <i>Gd. extremus</i> / <i>Gt. plesiotumida</i> ISZ											
M12		<i>P. mayeri</i> - <i>N. acostaensis</i> IZ			N15					AN 6	<i>Gt. scitula</i> PRZ		Tortonian
M11		<i>Glb. nepenthes</i> / <i>P. mayeri</i> Conc. RZ			N14								
M10		<i>Gt. F. robusta</i> - <i>Glb. nepenthes</i> IZ			N13		<i>Gt. peripheroronda</i> - <i>Glb. nepenthes</i> IZ						
M9	b	<i>Gt. f. robusta</i> ToT. RZ		<i>Gt. f. lobata</i> - <i>Gt. f. robusta</i> IZ	N12								
	a	<i>Gt. f. lobata</i> Lin. Z				N11	Mt7						
M8		<i>Gt. foehsi</i> s.s. Lin. Z											
M7		<i>Gl. peripheroacuta</i> Lin. Z			N 10	Mt6	<i>Orb. suturalis</i> / <i>Gt. peripheroronda</i> Conc. RZ			AN 4	<i>Gt. miozea</i> PRZ		
M6		<i>O. suturalis</i> - <i>Gl. peripher.</i> IZ			N9	Mt5	b	<i>Pr. glomerosa</i> - <i>O. suturalis</i> ISZ		<i>Pr. scana</i> - <i>O. suturalis</i> IZ			Langhian
M5	b	<i>Pr. glomerosa</i> - <i>O. suturalis</i> ISZ		<i>Pr. scana</i> - <i>O. suturalis</i> IZ	N8								

Fig. 7 Examples of planktonic foraminiferal biozonal schemes. Note the loss of biostratigraphic resolution with increasing latitude. In general, maximum biozonal resolution is obtained at low latitudes where species diversity is highest. Species diversity decreases with increasing latitudes, resulting in the loss of marker species in high-latitude stratigraphies. In this example of middle Miocene to lower Pliocene planktonic foraminiferal zonations for different latitudes, more than half of the biohorizons are lost between low and high latitudes. The upper Serravallian–lower Tortonian stratigraphic interval can be subdivided into seven zones and eight biozones at low latitude (M7–M13) but in only three biozones at mid latitudes and one biozone at high southern latitudes (Modified from Berggren et al., 1995, Fig. 5)

(Backman and Shackleton, 1983, Fig. 11), where abundance patterns help determine reliable biohorizons. The methodology is broadly applied but encourages a cumbersome terminology that may obscure its benefit (Table 7). It also raises a conundrum. If the typological definition of species is used in biostratigraphy and if the intraspecific variability of species is not known, how can abundance patterns be reliable? There can only be a large amount of subjectivity involved in taxonomic determination. This will need to be addressed, particularly in view of the existence of pseudocryptic species (Fig. 12).

Table 5 Strengths and weaknesses of specific types of biozones (From Hedberg 1976; Salvador, ed., 1994; North American Commission on Stratigraphic Nomenclature, 2005)

Biozone type	Definition	Strength	Weakness
Taxon-range zone TRZ	= Range of a species	Presence of species required	
Concurrent-range zone CRZ	= Overlap between the older range of one species and the younger range of another species	Presence of both species required	
Lowest occurrence interval zone LOIZ	= Interval between the LO of a species and the LO of another species	One of the types needed between a TRZ and a CRZ Successions of LOIZ associated with times of increasing diversification	
Highest occurrence interval zone HOIZ	= Interval between the HO of a species and the HO of another species	Useful in drilled material. One of the types needed between a TRZ and a CRZ Successions of HOIZ associated with times of decreasing diversification	
Highest to lowest occurrence interval zone HLOIZ	= Interval between the HO of a species and the LO of another species	One of the types needed between a TRZ and a CRZ	Identification is difficult, based on the whole assemblage, if isolated sample is to be dated or if section encompasses only one or two zones
Partial range zone PRZ	= Partial range of a taxon between the HO of a species and the LO of another species	The introduction of a third taxon constrains the HLOIZ	
Lineage zone LZ	= Interval between the two phylogenetic transitions	Potentially best first-order means of chronostratigraphic correlations	Taxonomy may be subjective. Requires quantification of lineage between species
Abundance zone AZ	= Interval marked by the abundance of a taxon		Abundance may vary between regions; strict quantification is not possible

Biostratigraphy and Stratigraphic Interpretation

Biostratigraphy is not only the most readily available means of relative dating and correlation of sedimentary rocks, it is also the cheapest and the fastest. For this reason, micropaleontologists are the first specialists onboard ship or on-site to receive sediments retrieved from core catchers during scientific and industrial drilling. Biostratigraphy also provides control on the identification of iterative stratigraphic information such as magnetostratigraphy and sequence stratigraphy

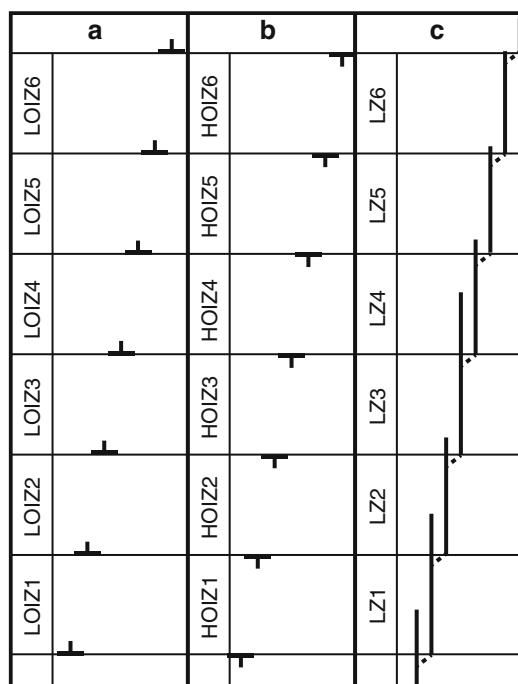


Fig. 8 Biostratigraphic zonations based on: (a) lowest occurrence interval zones, (b) highest occurrence interval zones, and (c) lineage zones. Any one type allows construction of a full biozonal scheme. This is different from concurrent-range zones and taxon-range zones that can only be used in combination with other biozones (Fig. 9)

(Fig. 13). At the same time, their integration results in significant refinement of biostratigraphic assignment and correlations (Fig. 13). This procedure is at the root of the ever-growing role of biostratigraphy in geochronology, which is the development of a chronology (a calendar indeed) in which biohorizons are converted into biotic events. In this manner, the LO and HO of species, both measured in terms of height/depth in a stratigraphic section, are converted into evolutionary events—e.g., evolutionary appearance and extinction—expressed in terms of dates (from which durations are derived). It is highly suitable that a dual terminology be used for biostratigraphy and biochronology, the former being the product of observation and the latter an inference (Fig. 14 and Table 8).

The fundamental problem in biostratigraphy is the temporal significance of biohorizons. Does every biohorizon record a specific event that can be singled out in the life span of a species? For instance, does every LO and HO correspond to, respectively, an FAD or an LAD? With Hedberg (1976, Ed., p. 63), we must recognize that “Biostratigraphic correlation is not necessarily time correlation.” This touches on the common problem of diachrony (=diachroneity) that has plagued biostratigraphy by casting doubt on its reliability. Diachrony concerns delayed LOs and premature HOs (or other biostratigraphic events) in stratigraphic sections (see McGowran, 2005, for a thorough discussion). The dispersal of species may not be instantaneous, or the geographic range of a species may contract or expand momentarily (Fig. 10). Latitudinal diachrony generally leaves a clear

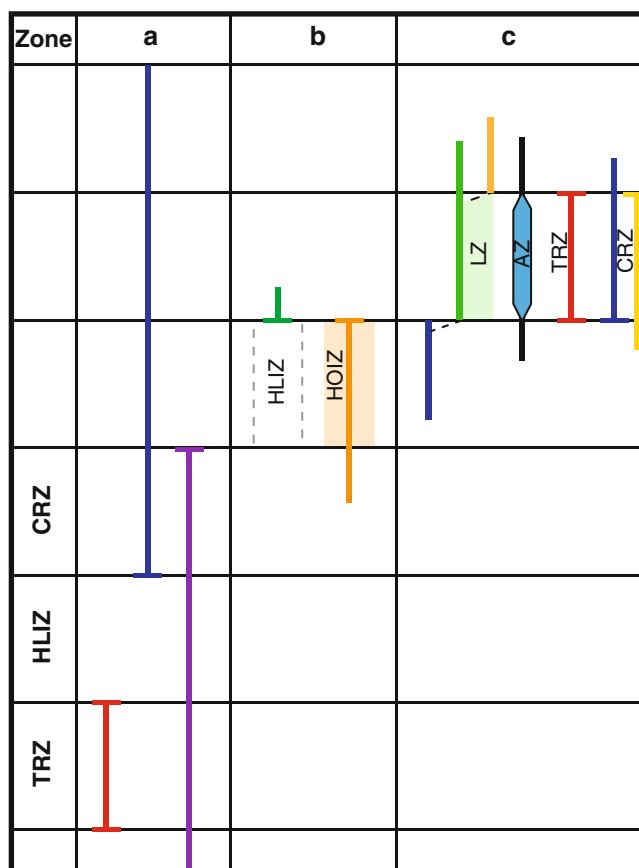


Fig. 9 Taxon-range and concurrent-range zones cannot be in consecutive order, but are necessarily separated by either a highest–lowest occurrence interval zone (HLOI zone, shown in *a*) or a partial range zone when only one zone separates them or by a combination of a HLOI and one lowest or highest occurrence interval zone when two zones separate them. An HLOI zone or a highest occurrence interval zone (*b*) necessarily intervenes between them and an overlying zone of any type (*c*). Note that LO in (*b*) might be the biohorizon defining the base of the taxon-range zone or the concurrent-range zone in (*c*)

Table 6 General difficulties encountered during biozonal correlations (Compiled from Pearson (1998))

Criteria	Problem	Consequences
Samples	Density is too low	Insufficient stratigraphic resolution
	Size is too small	Insufficient fossil recovery
Preservational biases	Fossils are scarce	Marker species are not found
	Extraction of fossils is very difficult	
	Preservation variable between beds in same section	Dissolution, abrasion, internal and external molds
	Variable between sections	
Displacement	Reworking	HOs are difficult to delineate
	Displacement by fluids	Dubious occurrences
Contamination	In the field	Anomalous occurrences
	In the laboratory	
	Downhole contamination during drilling	

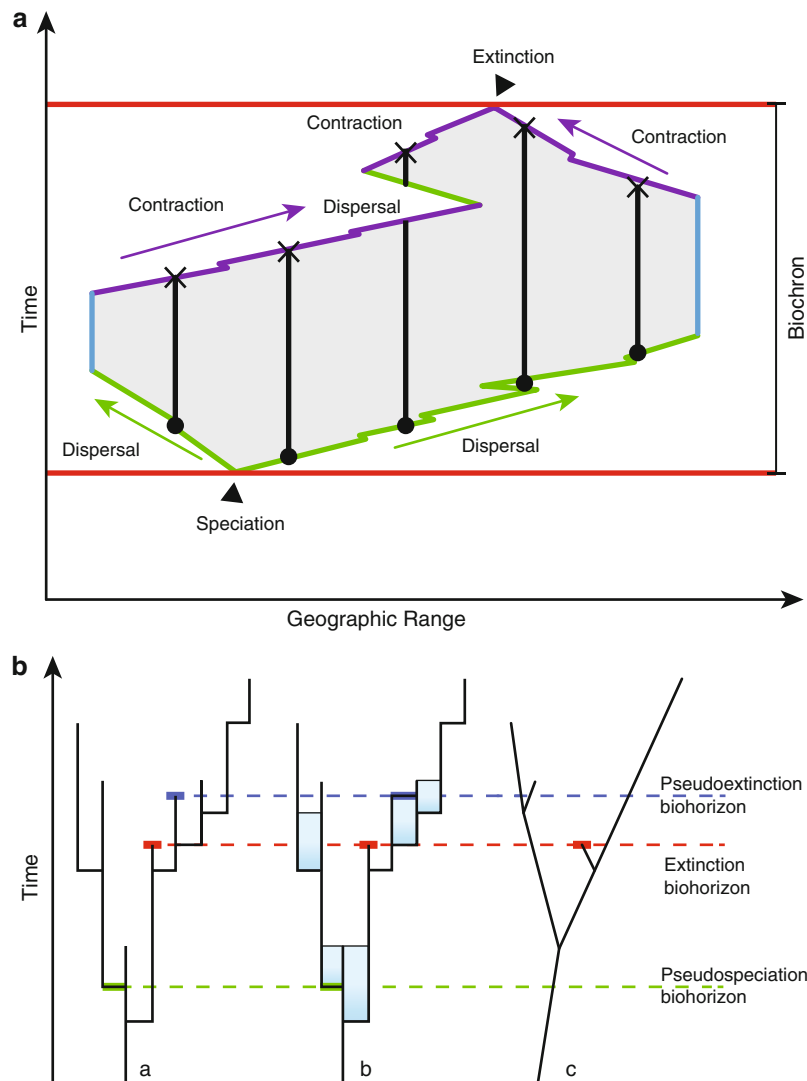


Fig. 10 Dispersal, extinction, pseudospeciation, and pseudoextinction biohorizons in a taxon-range zone (Modified after Pearson, 1996, Fig. 5.4 and 5.7). **(a)** Relationship of a taxon-range zone (species S) to space and time. Allopatric speciation of species S is followed by broad dispersal, itself followed by regional geographic stability or contraction, and finally geographic contraction until extinction of the species. In this model, the moment of speciation can only be known from one location; whereas the dispersal of the species constitutes a diachronous biohorizon (or a series of discrete biohorizons), as does the contraction of the biogeographic range. The extinction of species S is also known from a single location. **(b)** Possible relationships between typological species and evolutionary lineages. *(a)* As a first approach, ranges of morphospecies are linked in a dendrogram to show possible phylogenetic relationships. *(b)* Subsequent analyses show that transitional forms momentarily occur between morphospecies (*blue shading*). *(c)* Phylogenetic reconstructions, showing when cladogenetic and extinction events occurred. Combined, the cladogram and dendrogram allow distinction of pseudospeciation and pseudoextinction events that, although meaningless with regard to evolutionary patterns, may be useful as biohorizons

signature, and it involves long durations measurable in million years (Table 9), whereas ecological diachrony related to different water masses is of less amplitude. Tests allow determination of diachrony (Fig. 15), and orbital chronology is used to measure it (Table 9).

Diachrony is a rationalized process that immediately comes to mind to explain unexpected biostratigraphic patterns. However, unconformities produce patterns that mimic diachrony

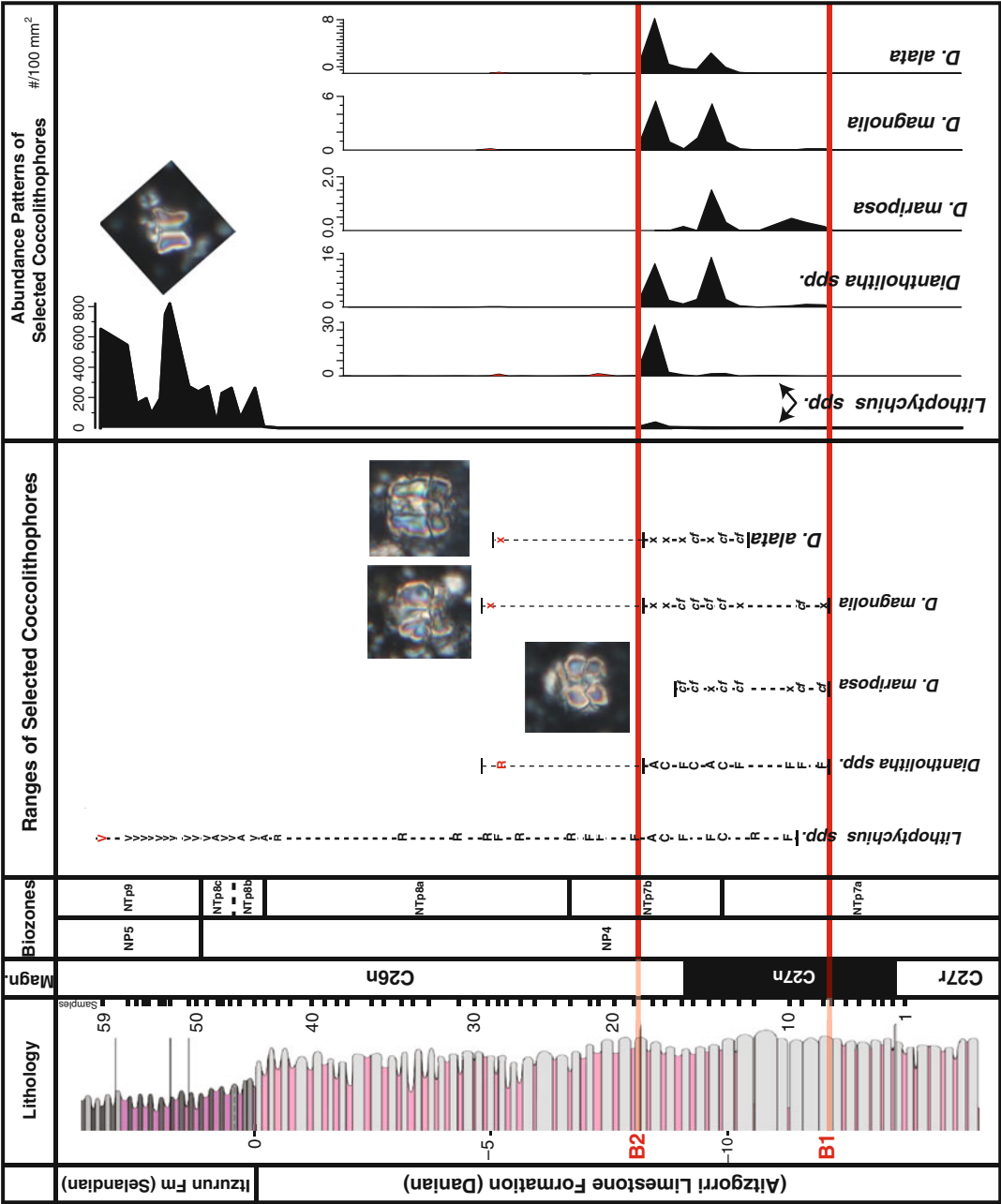


Fig. 11 Abundance patterns of coccoliths of the genera *Diantholitha* and *Lithoptychius* in the upper Danian section at Zumaia, Spain. Abundance patterns may be expressed as number of specimens/area (of a smear slide, prepared in a way similar to a blood sample) or as percentage of a species in a whole assemblage. Note that the same biohorizons are delineated based on qualitative and semiquantitative methods when the qualitative analysis has been rigorous. Red crosses: reworked specimens. Note that species may be rare in the lower part of their range (Data from J. Criscione, personal communication, January 2014)

Table 7 Biohorizons defined on the basis of abundance patterns

Biohorizon	Acronym	Definition
Highest occurrence	HO	Youngest horizon where the species has been recorded
Highest common occurrence ^a	HCO	Horizon above which the species does not occur consistently (continuous and/or common)
Reentrance ^a	RE	Horizon where a species re-occurs
Temporary high occurrence ^b	THO	Level above which a species is anomalously absent
Crossover in abundance	X	Shift in dominance of one taxon relative to another
Paracme end ^a	PE	Horizon below which a species is temporarily absent or present with scattered single specimens
Paracme end ^a	PB	Horizon above which a species is temporarily absent or present with scattered single specimens
End of acme ^a	AE	Horizon below which a species exhibits peaks in abundance
Beginning of acme ^a	AB	Horizon above which a species exhibits peaks in abundance
Lowest common occurrence ^a	LCO	Horizon above which the species occurs consistently (continuous and/or common)
Lowest continuous common occurrence ^c	LCtO	Horizon above which the species occurs consistently but in low to very low numbers
Lowest rare occurrence ^c	LRO	Horizon above which the occurrence of the species is rare
Lowest occurrence	LO	Oldest horizon where the species has been recorded

^aRaffi et al. 2006

^bFornaciari et al. 2010)

^cMonechi et al. 2013

(Aubry, 1995, Fig. 16), and failure to decipher unconformities leads to misinterpretation of biohorizons, which leads, in turn, to miscorrelation and incorrect age assignments and dating. Methodologies in two categories have been devised to delineate unconformities in stratigraphic sections. The first category, reviewed by Gradstein (2004), comprises deterministic and probabilistic quantitative methods that are applicable to all Phanerozoic stratigraphies and are generally used where classical biostratigraphic means are not applicable, in particular in industry. Graphic correlation (Shaw, 1964; Edwards, 1984) is classical among them (Fig. 17). The other methodologies are based on the analysis of sedimentation rates curves, in which terraces are indicative of stratigraphic gaps (Fig. 18). Terraces are formed at stratigraphic levels where LOs and HOs are juxtaposed although they markedly differ in age. This is at the origin of the method of temporal interpretation (Aubry, 1995) in which stratigraphic sections are projected into a temporal framework so that the duration (hiatus) represented by unconformities is fully accounted for.

The best documentation of evolutionary histories concerns the planktonic protists, and this can be attributed to their abundant, generally well-preserved, broadly distributed (the ocean occupies ~70 % of the surface of the planet) fossil record. In contrast, reconstitution of the evolutionary history of marine invertebrates and, to a lesser extent, benthic protists, has been problematic, largely because of their narrow dependence on specific environmental parameters. Their paleontologic records are biased by several factors, including artificial range truncation and stratigraphic gaps,

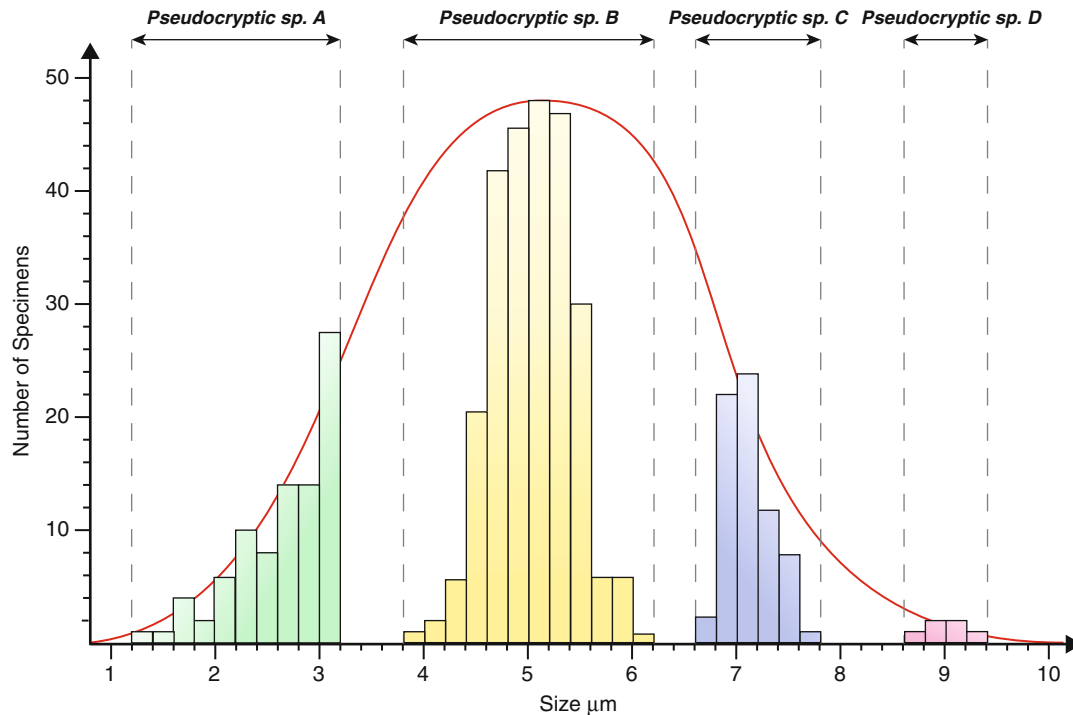


Fig. 12 Species and pseudocryptic species. Integrated morphologic and genetic studies of coccolithophores have shown that living species are in fact an aggregate of several pseudocryptic species (e.g., Saez et al., 2003; Hagino et al., 2009). This implies that the broad intraspecific variability attributed to single extinct taxon may in fact represent the cumulative variations of several extinct pseudocryptic species (the extinctions of which may constitute the pseudospeciation biohorizons of Pearson, 1998). Size may be a good indicator of pseudospeciation. Counts according to size class minimize the subjectivity involved in semiquantitative analysis of abundance patterns

which has led to formulation of models to predict their evolutionary patterns (e.g., Signor and Lipps, 1982; Holland, 1995; Springer, 1990). The method of temporal interpretation has permitted illustration of the role of unconformities in altering the record of paleobiological events as suspected by paleontologists and has shown that temporal resolution does not necessarily match stratigraphic resolution (Fig. 19). It has also strongly indicated that unconformities at sequence boundaries on continental margins extend to the deep sea (Aubry, 1991; 1995), which has notable implications for the documentation of paleobiological events among marine invertebrates (Fig. 20). Sequence stratigraphy postulates that the hiatus associated with sequence boundaries decreases along a coast to basinal transect so as to be nonexistent at the correlative conformity (e.g., Van Wagoner et al., 1998; Catuneanu et al., 2009). If the model of sequence stratigraphy is correct in this, paleobiological studies along depth transects on continental margins will help verify or supplant

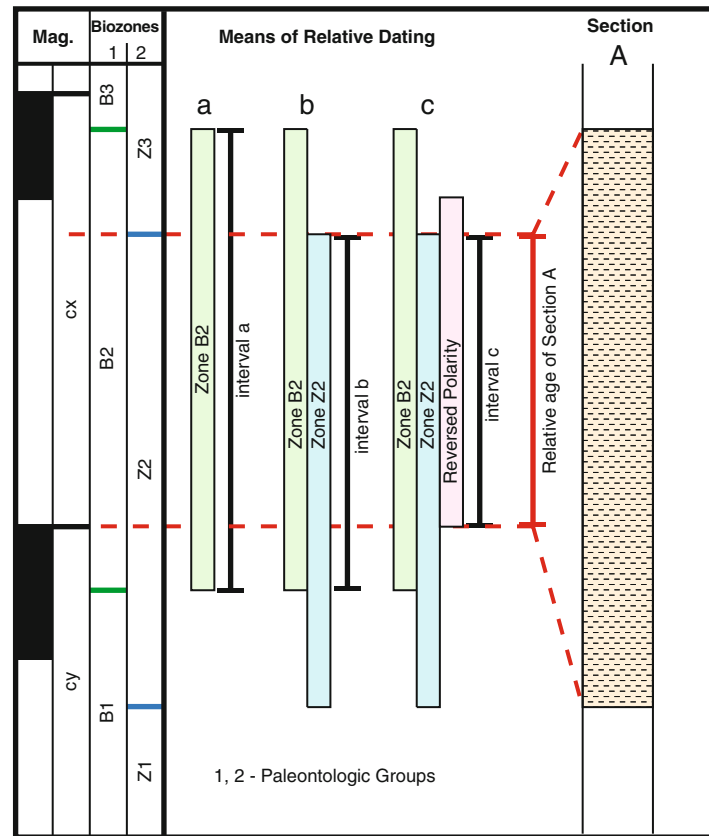


Fig. 13 Integration of magneto- and biostratigraphy. Although magnetic reversals occurred iteratively through time, each can be characterized by a particular species or group of species that existed or coexisted only during individual magnetochrons. Thus, biozone B2 may be a taxon-range zone defined by species A that lived only from late Chron Cyn to mid Chron Cxn. Assignment of a magnetozone associated with this biozone to any other chronal succession would be erroneous. In turn overlap between stratigraphic means allows to determine more precisely the relative age of the section. Based on paleontological group 1 alone (*a*), the section covers interval Ia; based on integration of paleontological groups 1 and 2 (*b*), it covers only interval Ib; adding magnetostratigraphy (*c*), it is reduced to interval Ic

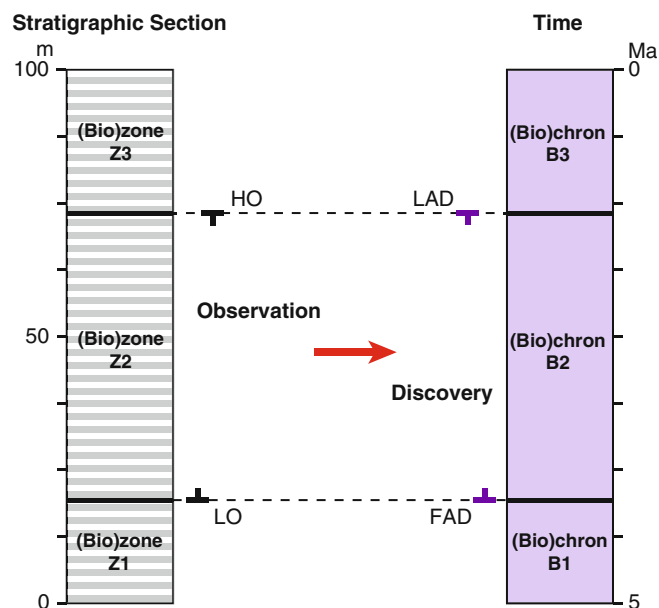


Fig. 14 Relationship between rock and time

Table 8 Biostratigraphic and biochronologic terminology. The dual stratigraphic versus temporal terminology shown here is recommended although it is not always followed. The term “biohorizon” is also referred to as surface, horizon, level, limit, boundary, band, marker, index, datum, datum plane, and key horizon. First and last appearance data (FAD, LAD) are commonly used in synonymy with biohorizon. However, *first* and *last* are temporal terms (in opposition to *lower* and *upper* that are stratigraphic terms) and are more appropriately used to designate temporal events, such as evolutionary appearance and extinction (see discussion in Aubry (1995) and (2007))

Stratigraphic terminology	Temporal terminology	
<i>Terms</i>	<i>Terms</i>	<i>Synonyms</i>
Biozone	Biochron	
Biohorizon	Bioevent	
Highest occurrence (HO)	Last appearance datum (LAD)	Extinction of taxon
	Last occurrence datum (LOD)	Cases of pseudoextinction
Lowest occurrence (LO)	First appearance datum (FAD)	Evolutionary appearance of a taxon
	First occurrence datum	Dispersal, cases of pseudospeciation
Abundance	Acme	
Stratigraphic event	Evolutionary event	Speciation, extinction, cladogenetic divergence
	Biogeographic event	Contraction/expansion of geographic distribution
Range	Span	

Table 9 Examples of diachrony exhibited by species of planktonic foraminifera (Wade et al., 2011) and coccolithophores (Backman et al., 2012; Raffi et al., 2006; Aubry, 1992). For reference (Raffi et al., 2006), only reliable (“A”) data are cited. Note that although ages in different works cited are based on different time scales and should not be compared, the amplitude of diachrony varies little between time scales. *LOD* last occurrence datum, *FOD* first occurrence datum, *EM* Eastern Mediterranean; (Aubry, 1992): latitudinal diachrony. Other works: different water masses at low latitude sites (Wade et al., 2011; Backman et al., 2012; Raffi et al., 2006; Aubry, 1992)

Datum	Age area 1 (Ma)	Age area 2 (Ma)	≠ (kyr)	Age area 3 (Ma)	≠ (kyr)	References
LOD <i>Dentoglobigerina altispira</i>	Atlantic: 3.13	Pacific: 3.46	330			Wade et al., 2011
LOD <i>Sphaeroidinellopsis seminulum</i>	Atlantic: 3.16	Pacific: 3.57	410			Wade et al., 2011
FOD <i>Globorotalia tumida</i>	Atlantic: 5.63	Pacific: 5.51	120			Wade et al., 2011
FOD <i>Nickilithus amplifucus</i>	Site 844B: 6.83	Site 845A: 6.75	80			Backman et al., 2012
FOD <i>Amaurolithus primus</i>	Atlantic: 7.39	844B: 7.38	40	845A: 7.42	40	Backman et al., 2012
FOD <i>Discoaster berggrenii</i>	Atlantic: 8.20	844C: 8.43	23	845: 8.56	36	Backman et al., 2012
LOD <i>Pseudoemiliania lacunosa</i>	Atlantic: 0.440	Pacific: 0.436	40	EM: 0.467	31	Raffi et al., 2006
LOD <i>Eudiscoaster brouweri</i>	Atlantic: 1.926	Pacific: 2.06	134	EM: 1.950	90	Raffi et al., 2006
LOD <i>Reticulofenestra pseudoumbilicus</i>	Atlantic: 3.81	Pacific: 3.79	80	EM: 3.839	49	Raffi et al., 2006
LOD <i>Eudiscoaster quinquereamus</i>	Atlantic: 5.54	Pacific: 5.59	50	EM: 5.54	50	Raffi et al., 2006
LOD <i>Amaurolithus amplifucus</i>	Atlantic: 5.978	Pacific: —		EM: 5.939	39	Raffi et al., 2006
FOD <i>Amaurolithus primus</i>	Atlantic: 7.362	Pacific: —		EM: 7.424	62	Raffi et al., 2006
LCO <i>Eudiscoaster kugleri</i>	Atlantic: 11.578	Pacific: —		EM: 11.596	18	Raffi et al., 2006
LCO <i>Reticulofenestra floridana</i>	Atlantic: 13.334	Pacific: 13.294	40	EM: 13.283	51	Raffi et al., 2006
LOD <i>Sphenolithus delphix</i>	Atlantic: 23.065	Pacific: —		EM: 23.089	24	Raffi et al., 2006
FOD <i>Sphenolithus delphix</i>	Atlantic: 23.328	Pacific: —		EM: 23.356	28	Raffi et al., 2006
LOD <i>Reticulofenestra umbilicus</i>	LL: ~32.3	HL: ~31.3	1			Aubry, 1992
LOD <i>Ericsonia formosa</i>	LL: ~32.8	HL: ~39.7	6.9			Aubry, 1992
LOD <i>Heliodiscoaster saipanensis</i>	LL: ~34.2	HL: ~35.4	1.2			Aubry, 1992
LOD <i>Heliodiscoaster barbadiensis</i>	LL: ~34.3	HL: ~39	4.7			Aubry, 1992
LOD <i>Reticulofenestra reticulata</i>	LL: ~35	HL: ~36.1	0.9			Aubry, 1992

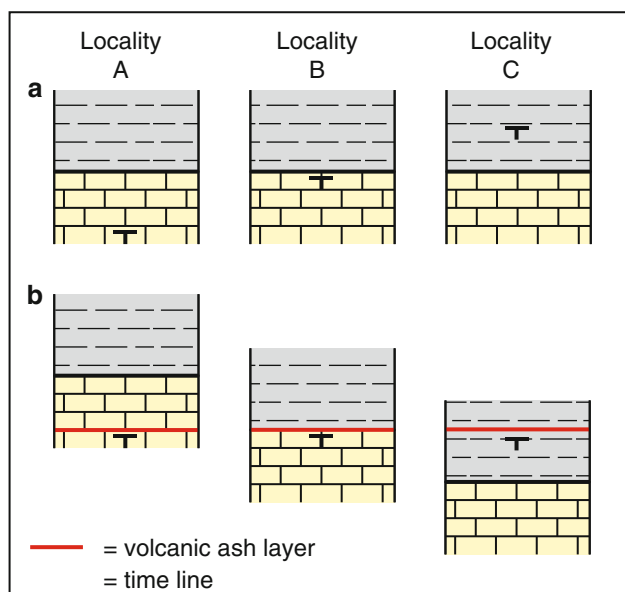


Fig. 15 Testing for diachrony. In this classic example, a paleontological event (extinction event) is considered diachronous because of its inconsistent relationship to a formational boundary (a). However, the finding of an ash layer of characteristic mineral composition (one of the shortest possible time markers) indicates that the extinction level is synchronous, whereas the lithological contact is diachronous (b)

models of evolutionary patterns (Fig. 19a, b). However, if the model of sequence stratigraphy is incorrect with regard to the decreasing hiatus down dip, tests of evolutionary models through studies of selected transects will not yield decisive information (Fig. 19c).

Conclusions

Biostratigraphy is the only non-iterative method of relative dating. Based on firm foundations, capable of evolving through the developments of new techniques, the rise of new concepts and their integration with other stratigraphic means it is the most dependable means of stratigraphic correlation and dating available to the stratigrapher. It is at the root of biochronology, and it makes possible insights into the rates at which earth and life processes occur on geological time scales. As such it is a major part of the framework upon which the history of the Earth system is being deciphered.

Some immediate and fundamental problems that biostratigraphy can help address concern the completeness of stratigraphic sections. Although Ager (1973) cautioned that the sedimentary record is highly discontinuous everywhere, overconfidence is increasing, unchallenged, that

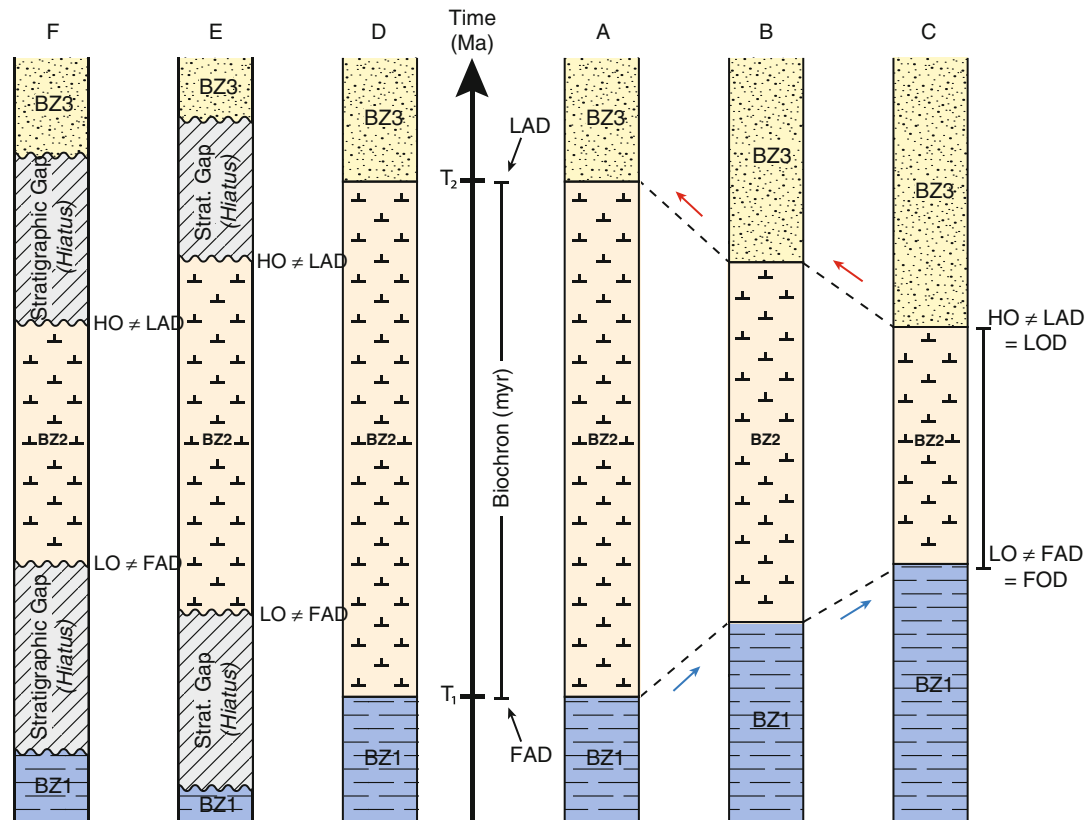


Fig. 16 Comparison between diachronous stratigraphic patterns and patterns resulting from unconformities (Modified after Aubry, 1995). Consider six sections (A–F) assigned to biozones BZ1 to BZ3, zone BZ2 being a taxon-range zone defined by the range of the planktonic species *Aglae xanthos*, which is abundant and equally well preserved in all sections. Zones BZ1 and BZ2 are interval range zones. *Aglae xanthos* had a life span of 2 Myr, between its FAD at 54 Ma (=T₁ in figure) and its LAD at 52 Ma (=T₂; FAD and LAD as defined in Table 8). The range of *A. xanthos* in section A represents the whole life span of the species, so that the LO and HO in the section correspond to the FAD and LAD of the species, at 54 and 52 Ma, respectively. The LO of *A. xanthos* is delayed in section B and even more in section C, whereas its HO occurs prematurely in the two sections, so that neither stratigraphic event corresponds to the FAD and LAD of the species. The LO is <54 Ma in section B and >> 54 Ma in section C, and the HO is >52 and >> 52 Ma in sections B and C, respectively. This stratigraphic pattern is typical of diachrony, the delayed occurrence in sections B and C corresponding to dispersal following evolutionary divergence or to ecologically forced expansion of the species, whereas the premature regional extinction results from contraction of the geographic distribution of the species. *Algae xanthos* exhibits a stratigraphic pattern in sections D to F that mirrors the diachronous pattern in sections A to C, but this latter results from truncation of its stratigraphic range in sections E and F. The important point here is that the biohorizons in sections B and C have significance with regard to the evolutionary and/or biogeographic history of the species and represent regional events (first and last occurrence), whereas the same biohorizons in sections E and F do not carry any evolutionary or paleobiogeographic significance. Blue arrow indicates migration; red arrow indicates contraction of biogeographic distribution

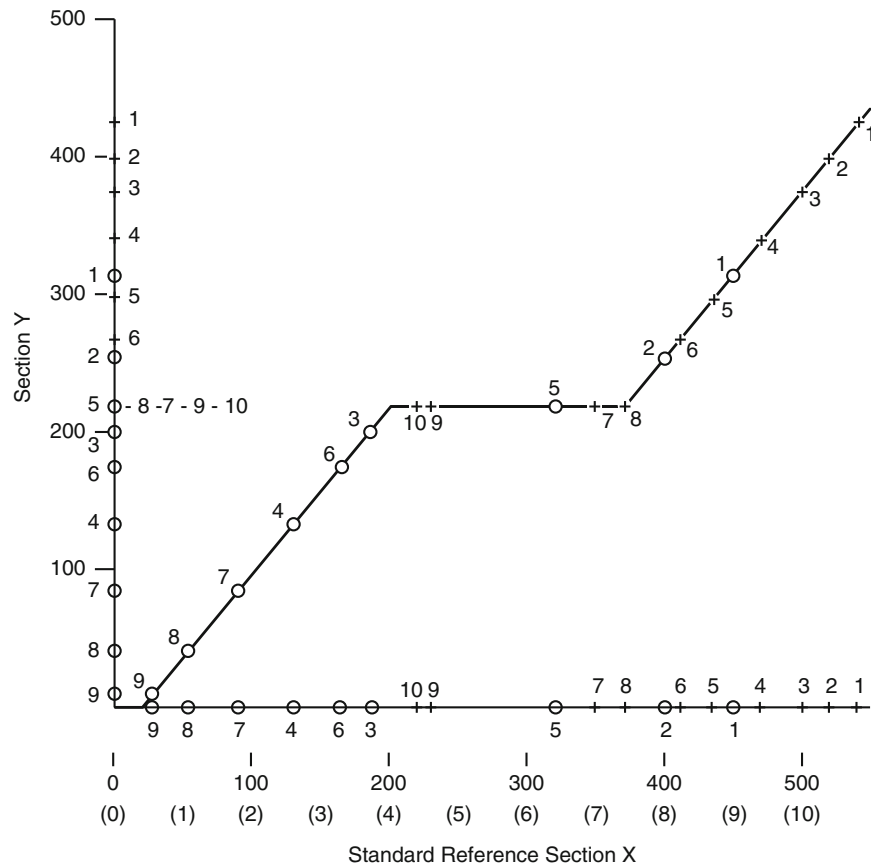


Fig. 17 Method of graphic correlation. Distance between stratigraphic events in a section is compared to their distance in a standard reference section. Note the terrace indicative of a stratigraphic gap. Numbered *circles* and crosses represent LOs and HOs, respectively [base and top in the method] (Modified from Miller, 1977, Text-Fig. 5)

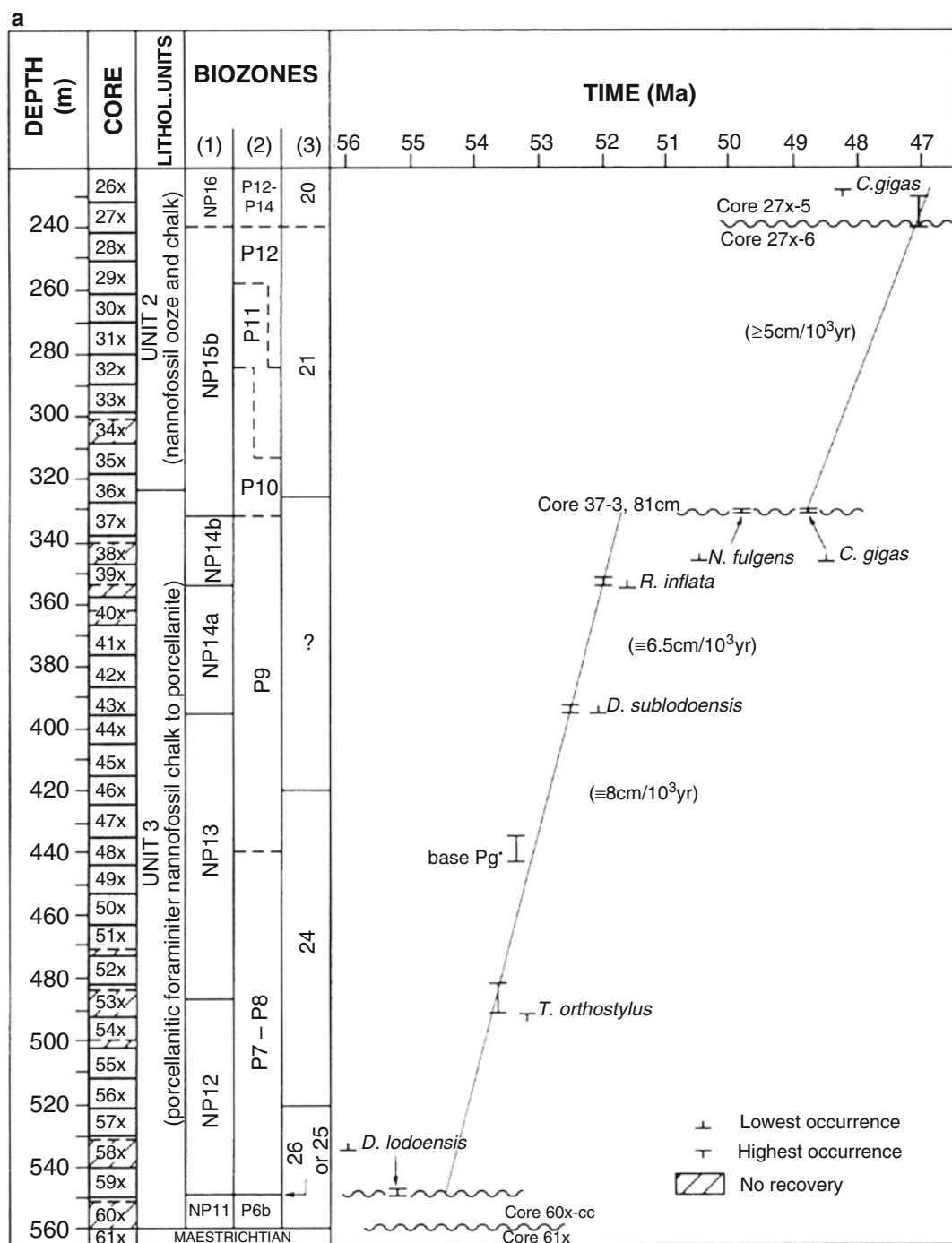


Fig. 18 (continued)

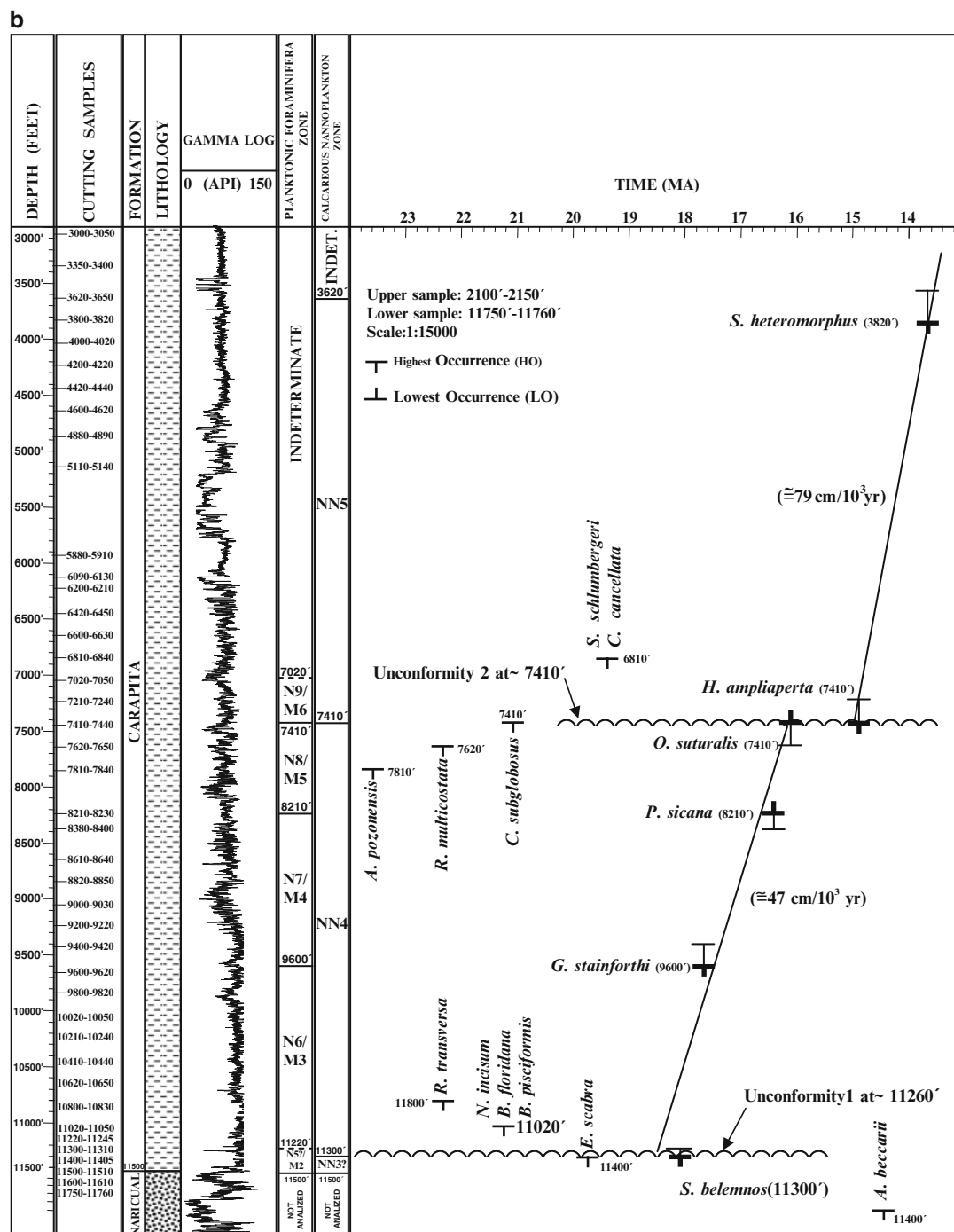


Fig. 18 Method of sedimentation rate curves. Sedimentation rate curves are constructed by comparing thickness between biostratigraphic events to duration between biochronologic events. When sedimentation is continuous, the thickness of biozones is essentially proportional to duration, and changes in rates result in changes in the slope of the curves. Stratigraphic gaps are marked by terraces (as in graphic correlation) corresponding to the overlap at the same stratigraphic level of multiple biohorizons. (a) Lower–middle Eocene section recovered from Deep Sea Drilling Site 612 (From Aubry, 1995) and (b) lower–middle Miocene section from an exploration well (From Sanchez et al., 2014)

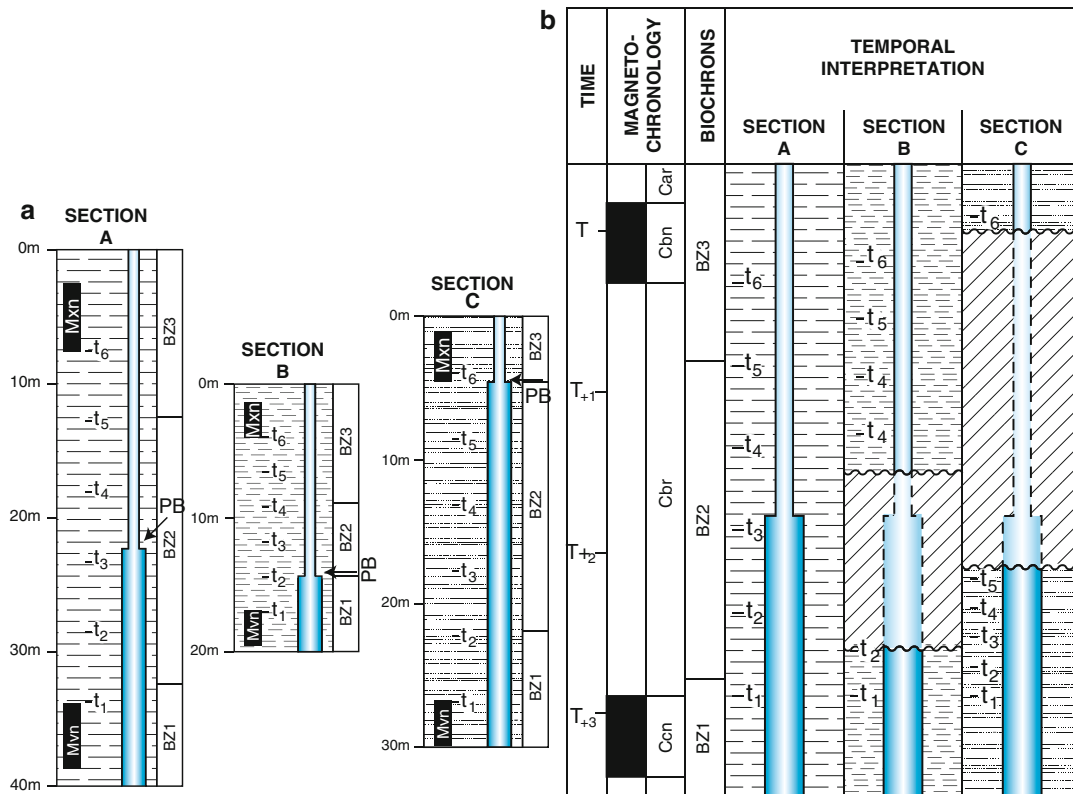


Fig. 19 Stratigraphic resolution versus temporal resolution and pseudo-diachrony. Consider three stratigraphic sections of different thicknesses, exhibiting a major paleobiological event [PB]. PB occurs in zone BZ2 in *sections A and B*, but in the middle of the zone in *section A* and in its lower part in *section B*. PB occurs at the BZ2/BZ3 zonal boundary in *section C*. Whereas at face value event PB is diachronous, temporal interpretation (cf. Fig. 18) of the sections using integrated magnetobiostratigraphy shows that correlative unconformities in *sections B and C* and associated with different hiatuses are responsible for apparent diachrony. Note also that the temporal resolution considerably differs in the three sections (Modified from Aubry, 1998, Fig.)

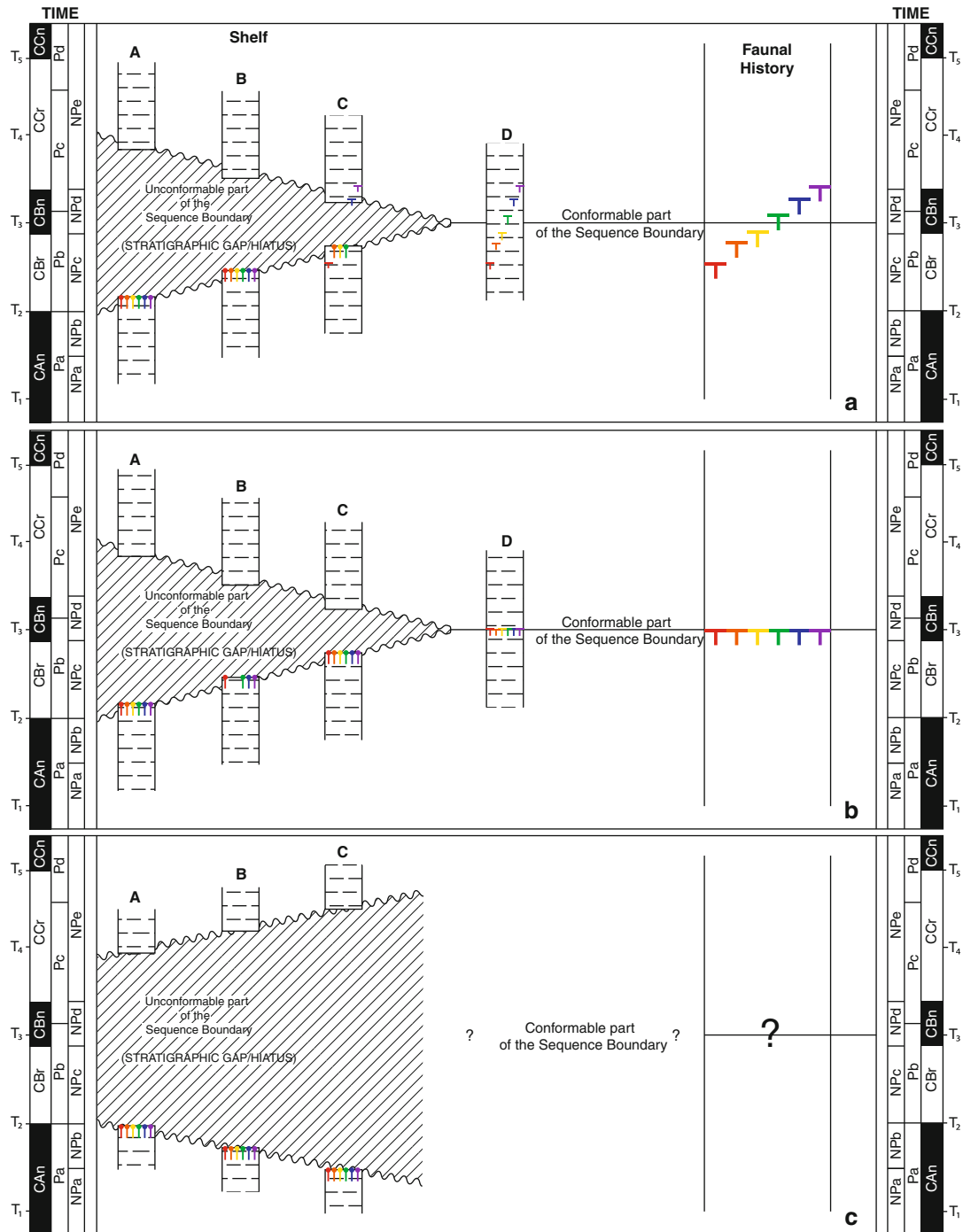


Fig. 20 Integrated magnetobiostratigraphic studies of sections carefully located along the sequence boundaries should, in principle, help resolve evolutionary patterns among organisms living on epicontinental shelves. In this example, if the hiatus associated with a sequence boundary decreases basinward, study of a continuous (temporally complete) section across the correlative conformity will allow determination of stepwise (a) or abrupt (b) extinctions. However, if the hiatus increases or remains constant basinward, the event cannot be constrained (c)

biostratigraphic records are reliable markers of time, seismic patterns are chronostratigraphic, and evolutionary modes of life can be restored from direct recovery of stratigraphic patterns and without tests of temporal continuity. These are fundamental questions that biostratigraphic studies must continue to address in the future.

Acknowledgments

I am most grateful to Jack Rink for inviting me to contribute to this entry on biostratigraphy; to W. A. Berggren, D. Bord, P. N. Pearson, W. Si, and J. A. Van Couvering for the discussion and their review of this entry; and to Sarah Klingler for the artwork.

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Uranium–Lead Dating

Randall Parrish*

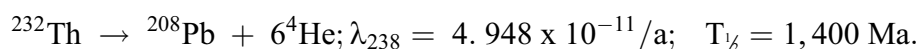
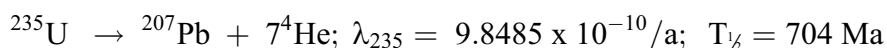
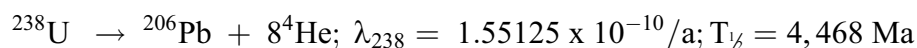
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Definition

Uranium–Lead dating is the geological age-determination method that uses the radioactive decay of uranium (U) isotopes (^{238}U , ^{235}U , and also in this entry ^{232}Th) into stable isotopes of lead (Pb) (^{206}Pb , ^{207}Pb , and ^{208}Pb , respectively). U–Pb geochronology is the science of both the methodology but also the application of these methods to geological problems.

U–Pb Decay System and Age Calculations

The accumulation of Pb in U-bearing minerals according to known decay rates of radioactive parent isotopes of U and Th forms the basis of this dating method. One measures the amount of *radiogenic* (i.e., produced from radioactive decay) Pb relative to the amount of radioactive parent isotope. As there are three radioactive isotopes (^{238}U , ^{235}U , and ^{232}Th) that decay into stable “daughter” isotopes of Pb, one can calculate three ages in this manner, two of which have the same (i.e., U and Pb) elements forming parent and daughter. The decay systems, decay constants (λ), and half-lives ($T_{1/2}$) are



The isotope ratio of uranium, $^{238}\text{U}/^{235}\text{U}$, has been recently determined to be 137.818 ± 0.045 (Hiess et al. 2012); a compilation of data from Hiess et al. (2012) from all terrestrial materials shows a variation from 137.71 to 137.96 with low-temperature earth materials having distinctly more variation as a result of the oxidation characteristics of uranium.

There are a number of intermediate isotopes in the decay chain that must first decay before stable Pb isotopes are produced. The most important ones for U–Pb dating are ^{234}U and ^{230}Th in the ^{238}U decay system and ^{231}Pa in the ^{235}U system, all of which have half-lives between 30,000 and 250,000 years. These intermediate isotopes produce complications to the interpretation of U–Pb dates that can be very important for young (i.e., Neogene) ages and particularly minerals with high Th/U such as monazite or allanite. Also there are a few cases where the effects are very dramatic and

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which may involve ^{231}Pa excesses in the ^{235}U – ^{207}Pb decay chain (Oberli et al. 2004; Anczkiewicz et al. 2001).

The basic age equation is

$$T = (1/\lambda) * \ln(1 + D/P),$$

where T is the age, D refers to a molar quantity “daughter” isotope of Pb (^{206}Pb , ^{207}Pb , and ^{208}Pb), and P refers to the respective molar quantity of a parent isotope of Uranium (or Thorium), and where λ is the decay constant for each respective radioactive parent isotope (^{238}U , ^{235}U , ^{232}Th).

Published studies have used this dating system for materials ranging from the age of the solar system (4,567 Ma) to less than 1 Ma. A unique aspect of this decay system is that the two parent isotopes of U, with contrasting decay constants, become two isotopes of Pb; as a result, the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ isotope ratio is a strong function of age, and it can be used to provide an additional date, based on the measured radiogenic Pb isotope ratio alone. This Pb isotope ratio can be measured very precisely, and this property allows uncertainties for ancient samples to be much smaller than would otherwise be the case, as little as 1 part in 10,000 of the age of a sample. The equation for this Pb isotope age calculation is:

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}} = \frac{^{235}\text{U}}{^{238}\text{U}} * \frac{\exp(\lambda_{235}T - 1)}{\exp(\lambda_{238}T - 1)},$$

where T is time and $^{235}\text{U}/^{238}\text{U}$ is the current isotope ratio of uranium ($= 1/137.818$).

When the measurements are made, dates are calculated by measuring a daughter/parent ratio ($^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, $^{208}\text{Pb}/^{232}\text{Th}$) and a radiogenic lead isotope ratio ($^{207}\text{Pb}/^{206}\text{Pb}$), resulting in up to four calculated dates, three of which are part of the U–Th–Pb system of decay.

In the U–Pb system, a calculated date using one of the equations above does not necessarily result in the most valid interpreted age of a mineral, partly because some minerals have a tendency to lose Pb as a result of volume diffusion and/or diffusion via radiation damage and partly because some accessory minerals can have multiple age components during their formation (e.g., cores overgrown by younger rims). These combined effects are often referred to as “open-system” behavior, referring to cases where a date does not simply reflect a single growth domain where the parent and daughter isotope ratio has changed only through radioactive decay. Age patterns within single grains of zircon and monazite, in particular, can be quite complicated because of these factors and require careful analysis in the petrographic context, especially in metamorphic rocks (Cottle et al. 2009).

A method of visually displaying measured isotope ratios to better interpret potential complexities resulting from open-system behavior can be attributed to Wetherill (1956), who devised the Concordia diagram. This diagram graphically interrelates all three ratios of the U–Pb system whereby the X and Y axes are $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$, and the inverse gradient of any point drawn through the origin is proportional to $^{207}\text{Pb}/^{206}\text{Pb}$. In this diagram, a curve originating at the origin, termed the “concordia curve,” defines the $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ values where the calculated dates of these ratios are identical, using the age equations above. Any measured analysis of a mineral that plots within uncertainty of the Concordia curve is considered “concordant,” having its $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ calculated dates the same within uncertainty. If falling off this curve, either above or below, an analysis is termed “discordant,” with measured dates not in agreement.

A variant of the Concordia diagram, termed the Tera-Wasserburg diagram (Tera and Wasserburg 1972), plots $^{207}\text{Pb}/^{206}\text{Pb}$ as Y and $^{238}\text{U}/^{206}\text{Pb}$ as X and is particularly useful when measurement of the small ^{204}Pb isotope is imprecise or not possible. Both of these diagrams offer a graphical method

of making a correction for disturbances to the U–Pb system arising, for example, from a single moment of Pb loss or a second phase of mineral growth well after a mineral's formation, in order to calculate the original time of mineral growth. Further variations of the Concordia diagram involve $^{208}\text{Pb}/^{232}\text{Th}$ plotted against $^{207}\text{Pb}/^{235}\text{U}$ or $^{206}\text{Pb}/^{238}\text{U}$ to illustrate behavior involving U, Th, and Pb isotopes. The use of two parent U isotopes and two daughter Pb isotopes is a very useful property; it allows a correction for disturbed systems and recovery of the initial age of a mineral, a feature unique to the U–Pb dating method among all isotope geochronometers.

A correction for initial or “common” lead, that is, the lead incorporated into a material at its time of formation, is implicit in calculation of ages. The theory of this is well-developed in many geochemistry or geochronology textbooks and is not detailed herein.

Historical Development of the Method

The discovery of radioactivity of uranium was a pivotal event, with recognition that transformation of uranium into other elements was inevitable. Early on, lead was suspected of being the ultimate stable end product of this decay (Boltwood 1907). Even before the discovery of isotopes by Frederick Soddy in 1913 (Soddy 1913), U–Pb ages of geological materials were calculated, using initial estimates of the half-life or decay rate of uranium. Although Boltwood (1907) was the first to calculate the age of a mineral based on its U–Pb ratio, Arthur Holmes (Holmes 1911), under the guidance of his supervisor R J Strutt, determined dates of a suite of igneous-related Devonian minerals of variable U–Pb ratio in Norway by measuring the atomic U–Pb ratio in minerals with improved methods. This study used a combination of appropriate geological samples with clever methods of classical wet chemistry and radiochemistry. The dates calculated, approximately 370 Ma, were within 5 % of the correct ages determined later. Holmes also recalculated Boltwood's dates with a better decay constant, having sought information on the geological context of Boltwood's samples from the US Geological Survey. These were of real importance because this began the first numerical calibration of the geological timescale as well as proving that the Earth was much older than 1 Ga.

The discovery of isotopes by Soddy had little impact initially to U–Pb dating because the development of mass spectrometry capable of measuring U or Pb isotopes was only achieved decades later. This changed dramatically in ~1935 with advances in technology. Alfred Nier, among the most brilliant of all mass spectrometrists of the twentieth century, designed instruments and ion signal amplification devices that could measure accurately and relatively precisely the isotope composition of U and Pb; indeed, his measurement of U isotopes were pivotal in demonstrating that ^{235}U was the isotope capable of fission by thermal neutron irradiation (Nier 1939). His measurements of Pb isotopes allowed U–Pb isotope ages of U ore minerals to be calculated and a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2.6 Ga to be determined on monazite (Nier et al. 1941). Some years later, Claire Patterson (1956) published accurate and precise measurements of primordial lead in troilite (an iron sulfide with negligible U) from the Canyon Diablo (Meteor Crater, Arizona) Ni–Fe meteorite that allowed an age of ~4.55 Ga for the age of early solar system meteorites to be established.

One of the most important collateral outcomes of atomic energy research was the accurate and precise method of isotope quantification known as isotope dilution. In this method a known quantity of an enriched isotope of an element (i.e., ^{235}U , ^{208}Pb) is added to a sample prior to dissolution, and the concentration of natural U and Pb isotopes in the sample are calculated using the measurement by mass spectrometry of the isotope composition of the resultant mixture. This method is an

extension of the original method using radioactive tracers invented by George de Hevesy in 1913, for which he was awarded the Nobel Prize in 1943.

This procedure is simple and superbly reliable. To illustrate how this works, imagine a bucket of unknown quantity of colored balls that are black and white in a ratio of 2:1 black–white (representing the natural isotopes in a sample). If one adds 100 red balls (representing the enriched tracer) and mixes the balls up and then measures a ratio of red–black of 0.5 (by isotope ratio mass spectrometry of a portion of the sample), then one can easily work out that there are 50 black and 25 white balls in the original sample. One does not have to count all the balls to know this; one only needs to know the number of tracer balls added and the ratio (i.e., isotope ratio) of the mixture.

This methodology was developed and applied to a wide range of elements and sample materials. It still represents the most accurate and precise manner of isotope quantification in geological samples. One of the finest early papers to date accessory minerals by these methods is the *tour de force* of Tilton et al. (1955) in which various minerals were dated in a Precambrian granite; the paper presents tedious but elegant analytical methods, including not just U–Pb but also Th–Pb, and is a required reading for all U–Pb geochronologists who wish to appreciate the fundamental work of the early pioneers of the methods we now use so routinely. This was the standard method of U–Pb geochronology until the mid-1990s and is still widely used today.

Evolution of Methods 1955–1980

In the isotope dilution method of U–Pb dating, decomposition of samples into a homogeneous solution is a requirement so that tracer and sample isotopes can fully mix prior to chemical separation and isotope analysis by mass spectrometry. During the period prior to ~1970, dissolution of various silicate minerals useful for U–Pb geochronology (i.e., zircon) was tractable only with flux melting followed by HCl acid dissolution, and it required a large quantity of sample material. This was a hindrance to widespread application of the U–Pb dating method partly because of the time and expense involved in the procedure but also because zircon commonly loses Pb due to radiation damage of its crystal lattice. When large quantities of zircon were analyzed by this flux method, this inevitably resulted in many discordant dates being produced because of the prevalence of Pb loss in some of the grains; analysis of tiny amounts of high quality zircon was simply not generally possible. This frustrating reality proved to be a strong motivation to find a better way – to be able to analyze much smaller quantities of zircon and ultimately single grains that were of very high quality not subject to significant Pb loss.

In the late 1960s and early 1970s, two young geologists – Tom Krogh and James Mattinson – devised a solution to this conundrum while doing work early in their careers at the Carnegie Institute of Washington. Using the availability of Teflon™, which fortuitously had been discovered by Roy Plunkett of DuPont Corporation in 1938 during refrigerant research, Krogh and Mattinson made several key breakthroughs in geochemical research: (1) the ability to dissolve refractory minerals like zircon in HF acid at high temperatures (~220 °C) in steel-jacketed Teflon™ pressure vessels, (2) the ability to clean Teflon™ vessels so as to introduce very little additional lead contamination, and (3) the development of sub-boiling distillation of acids in Teflon™ to produce ultrapure acids with low lead contamination. Together with the silica gel Pb ionization method on a re-thermal ionization filament, it became possible to analyze single grains of zircon or other minerals; a practice that is routine today. Despite these improvements, the issue of Pb loss in zircon still hindered high-precision age determination. Krogh (1982) addressed the problem of zircon discordance by inventing the air abrasion technique to remove the discordant outer part of

zircon crystals, which resulted in production of vastly improved concordance (i.e., closed-system behavior) of zircons. In 1985–1987, R Parrish worked with Tom Krogh and J C Roddick (Parrish and Krogh 1987; Roddick et al. 1987) to synthesize a significant quantity of the artificial isotope ^{205}Pb for distribution to world laboratories and devised an efficient method to dissolve multiple individual zircon samples in a single steel-jacketed pressure vessel. All of these analytical advances conspired to facilitate a very significant growth in the number of U–Pb laboratories and the quantity of high-accuracy, high-precision zircon dates. Using U–Pb zircon dating with $\leq \pm 4$ Ma uncertainty, Precambrian volcanic chronostratigraphy became a commonplace in the 1980s–1990s, especially in Canada. A great advance in Precambrian continental orogenic evolution then proceeded, especially in the Canadian Shield. This made possible seminal papers on continental evolution, such as Paul Hoffman's United Plates of America synthesis (Hoffman 1988).

At the same time, when these methods were applied to complicated igneous and metamorphic zircon, the complexity in zircon U–Pb systematics became apparent, including the phenomenon of zircon inheritance and multiple metamorphic zircon growth periods during high-grade metamorphism. In such cases, single-grain analysis produced consistently discordant data, and the determination of precise ages of metamorphism or igneous events proved to be a challenge in many samples. Complex zircon growth and alteration were imaged using electron microscopy, suggesting that the complexities in U–Pb data were the result of a combination of lead loss and multiple zircon age domains within single grains. The paper by Corfu et al. (2003) illustrates the variation in textures elegantly. The analysis of zircon on the micron scale became an obvious tantalizing goal, but it presented major technical challenges and was impossible at the time for multi- or single grain zircon analysis by ID-TIMS. One way forward using ID-TIMS came from accessory minerals like monazite with less inheritance and Pb loss to determine igneous and metamorphic ages (Parrish 1990).

With more work applied by ID-TIMS methods to alternative minerals, the effects of chemical fractionation of the intermediate daughter isotopes ^{230}Th and ^{231}Pa relative to ^{238}U and ^{234}U became better documented (Schärer 1984; Parrish 1990; Anczkiewicz et al. 2001). As a result of this effort on alternative minerals, excess ^{206}Pb in monazite and other Th-rich minerals, sometimes of huge relative magnitude, was documented, and smaller magnitude ^{206}Pb deficiencies and much more rare ^{207}Pb excesses (Anczkiewicz et al. 2001) were documented in zircon; all of these features were shown to exist by early work of Mattinson (1973).

Notwithstanding the advances made by laboratories using the ID-TIMS method, efforts to develop in situ methods of U–Pb analysis were accelerating, building on advances in secondary ion mass spectrometry (SIMS).

In Situ Methods of U–Pb Analysis

In this article, in situ U–Pb dating refers to the measurement of age of a mineral in a solid state using microbeam sampling techniques, and it includes first SIMS and later LA-ICP-MS methods, as well as the less-used electron microprobe chemical dating method, all of which are described briefly below.

Among other scientists involved in SIMS (secondary ion mass spectrometry) techniques, William Compston of the Australian National University (ANU) led a team to develop SIMS methods for the analysis of very small ($<50\text{ }\mu\text{m}$) regions of zircon for the purpose of U–Pb dating. The SIMS method consists of firing a primary highly focused ion beam (oxygen or cesium ions) onto the surface of polished zircon in order to produce secondary sample ions which are then accelerated and focused

into a beam which could be analyzed by a mass spectrometer. However, in SIMS zircon analysis, a wide range of molecular ions are produced during the primary sputtering process where the beam interacts with the sample. Many of these molecular ions have very similar masses in relation to the Pb isotopes that are of interest for dating, and which occur in very small quantities. In order to cleanly separate and measure the molecular ions from the Pb ions of interest, larger radius (>1 m) double-focusing high mass resolution SIMS instruments had to be designed and built. In the U–Pb trade, these methods have been loosely termed “ion microprobe” methods, and the ANU instrument was termed “SHRIMP” (Sensitive High Resolution Ion Microprobe) and was built in the early 1980s; an analogous instrument was built in France by Cameca Instruments in the early 1990s. In 1984, the first SIMS zircon age was published by Compston et al. (1984), and it determined an age of 4.36 Ga for zircons in lunar breccia sample 73,217 returned from Apollo 17. This development heralded a new period of exploration of zircon as a geochronometer, although the application of the SIMS zircon work to terrestrial rocks did not see wide application until the 1990s.

SIMS U–Pb methods cannot quantify accurately the ratio of Pb to U isotopes within a zircon or other accessory mineral directly. Instead calculation of a date relies on the analysis of a “standard” or “reference” zircon whose U–Pb isotope ratios must have been determined by the ID-TIMS method. Ion signals of unknowns are measured and compared to those of the reference zircons (the Pb–U ratio which is known) to establish a calibration relationship; this in turn is used to calculate the $^{206}\text{Pb}/^{238}\text{U}$ ratio of the unknown, then used for age determination. A series of zircon reference samples has evolved over the past ~30 years, with variable ages, U contents, homogeneity, and extent of concordance. The search for, and characterization of, suitable reference materials for isotopic and elemental analysis is an ongoing effort for in situ analysis, and not just for zircon.

Building on earlier work with quadrupole mass spectrometry and ionization using plasma sources, inductively coupled plasma ionization (ICP) was combined in the early 1990s with multiple-collector mass spectrometry (MC-MS) using an additional electrostatic analyzer to make the first ICP multi-collector mass spectrometer (ICP-MC-MS). This instrument combined the highly efficient ICP ion source with multiple collections of ion signals in a mass spectrometer of mass resolution similar to a normal TIMS instrument (mass resolution ~400). Shortly thereafter, laser ablation (LA) micro-sampling was attached to this type of instrument to deliver the first LA-ICP-MC-MS, with the measurement of U–Pb ages using a zircon reference sample. One of the more comprehensive early papers using this method was that of Horstwood et al. (2003) which also included a common Pb correction. Among other applications, this allowed hafnium (Hf) isotopes to be measured more time efficiently than by TIMS methods, and this was exploited by ID-TIMS zircon geochronologists to add Hf model ages to the zircon U–Pb evolution (Davis et al. 2005). These were the precursors to more widespread LA-ICP-MS instruments on the market now, which offer sufficient sensitivity and precision to compete directly with SIMS in situ analysis, but at less cost and with greater sample throughput, though with higher sample consumption. Both SIMS and LA-ICP-MS (including LA-ICP-MC-MS) instruments are dependent on one or more reference samples for date calculation.

SIMS U–Pb methods are very sensitive to surface polish quality and surface-charging characteristics and require a careful matching of the composition (matrix) of sample to the reference material. LA-ICP-MS methods, on the other hand, are more tolerant of surface irregularities, are less sensitive than SIMS methods to sample matrix matching, consume a larger quantity of sample, and have limited ability to measure the common Pb reference isotope ^{204}Pb due to the interference with ^{204}Hg in the carrier gas. Careful work using the most sensitive LA-ICP-MS methods, however, can deliver the same age accuracy and precision as SIMS methods with consumption of sample only a factor of 2–4× greater, with laser ablation pits as small as a few μm deep and ~20 μm in diameter. Depth

profiling by both methods is possible but is more controlled via SIMS analysis. As of the time of writing, international efforts are underway to improve interlaboratory inter-comparability of U–Pb data, but a fundamental limitation of both of these in situ methods is that accuracy and precision of the $^{206}\text{Pb}/^{238}\text{U}$ ratio in a sample appears limited to $\sim 1\text{--}2\%$ 2σ on weighted mean dates, which places a fundamental limit on the ultimate age precision measured by means of the $^{206}\text{Pb}/^{238}\text{U}$ ratio. The exact reason for this limitation is likely some combination of plasma chemical fractionation and laser ablation processes, perhaps compounded by matrix matching issues.

Unfortunately, a misunderstanding of the strengths and weaknesses of both isotope dilution methods and in situ SIMS or LA-ICP-MS methods traditionally led to tension between the two methodological communities. For example, SIMS dates claiming a precision of $<1\%$ of zircon age were published in numerous studies, and some were used to attempt a refinement of the geological time scale; several of these have been refuted and subsequently refined by careful isotope dilution methods. On the other hand, many papers contain published isotope dilution U–Pb zircon data that are discordant and yield non-unique and ambiguous interpretations of age on complex multiple growth-zoned zircons. More often than not, these complex and ambiguous interpretations are from metamorphosed rocks where multiple high-temperature events have produced complicated zircons. The primary lesson from these examples is that both methods have their strengths, and when used appropriately, rocks and events can be dated in the best possible way using one or both methods. All of these methods have their place in U–Pb geochronology.

Two further methodological aspects deserve mention. Electron microprobe U–Th–Pb analysis of monazite has been done since 1994 (Suzuki et al. 1994). This “chemical” (as opposed to isotope) method of dating was refined by Montel et al. (1996) and Williams and Jercinovic (2002) primarily in Precambrian rocks where monazite contains relatively large quantities of radiogenic Pb, sufficient to overwhelm any initial common lead, while preserving the petrographic context. Monazite U–Th–Pb *isotope* dating in thin sections is the only method able to reveal the ages of very young monazites of Mesozoic–Neogene age, however. Together, EMP, SIMS, and LA-ICP-MS methods offer significant insight into the P–T–t (pressure–temperature–time) conditions and paths of metamorphic rocks of all ages from Archaean to Neogene.

Two More Innovations to Remember

A further refinement was developed over many years by James Mattinson in a procedure loosely termed “chemical abrasion” or “CA-TIMS” (Mattinson 2005). Effectively this is a recipe involving high-temperature ($\sim 900^\circ\text{C}$) annealing of zircon, followed by a HF–HNO₃ acid partial dissolution of annealed grains, which effectively removes the discordant regions (zones, cracks, etc.) of a zircon grain, leaving undissolved zircon that has been a closed system since formation. When the residual zircon is analyzed, concordant analyses often result, allowing very precise concordant ages to be determined. This is such a profoundly important procedure that it has been adopted worldwide as the routine zircon procedure for ID-TIMS methods.

Finally, any U–Pb geochronologist will understand clearly the value in accurate and sophisticated data reduction, linear regression, and graphical plotting software to diversely illustrate and determine uncertainties in ages of U–Pb data, the latter being its most important attribute. The most commonly used software to plot data, termed Isoplot, was conceived, written and refined over several decades primarily by Ken Ludwig of the Berkeley Geochronology Center (Ludwig 1991). It is one of the most important underpinning tools that U–Pb geochronologists use.

Geologists and geochronologists, indeed humans in general, have a tendency to take for granted the technological advances that make our lives easier; it is important to remember the intellectual breakthroughs as well as the sheer effort of scientists who pioneered these advances. These breakthroughs have made the science of U–Pb geochronology as apparently routine as we know it today.

U–Th–Pb Geochronology: Applications to Earth, Planetary, and Environmental Science

Applications of U–Pb geochronology are incredibly varied, more so than with any other chronometer. Topics that have been addressed by U–Th–Pb geochronology include:

- The age of meteorites, the Moon, Earth, and the Solar System
- The age of igneous events throughout Earth history, plutonic and volcanic, mafic, alkaline, and felsic
- Earth differentiation and subsequent crustal evolution
- Age of the oldest continental crust and Earth materials
- The behavior of intermediate daughter radioactive isotopes and their impact on high-precision dating
- Rates of production of continental crust
- Continental reconstructions over time involving amalgamation and dispersal of continents
- Rates of tectonic events in arcs, collisional orogens, etc.
- Age of plumes and large igneous provinces and their global impacts
- Quantification of time in pressure–temperature paths of metamorphic rocks (P–T–*t* paths)
- Chronostratigraphy, in particular in Precambrian where biostratigraphy is absent
- Calibration of the geological time scale
- Rates of cooling of orogens and rocks by using U–Pb dates as *thermochronometers* in the context of closure temperatures
- Identifying the age of sources of igneous rocks by zircon and monazite inheritance
- Dating multiple growth zones in complex minerals even at micron-scale dimension
- Timing of diagenesis and cementation of sedimentary rocks
- Precise dating of extinction events facilitating the search for causality
- Dating of calcite and phosphate of Quaternary age for environmental reconstructions and human evolution
- Provenance of sediments, sedimentary rocks, dust, river sand, and ice-rafted glacial debris

Some of these topics are elaborated in chapters within this volume, but others are less well described. The following section highlights aspects of applications that are considered particularly interesting additions to complement the other chapters.

Minerals for U–Pb Dating

The inventory of minerals available for U–Th–Pb geochronology is vast; nearly any mineral that is capable of partitioning U or Th into its structure can be dated. The most commonly used minerals are, in approximate order of their use in geochronology:

- Zircon (ZrSiO_4)
- Monazite ($(\text{Ce}, \text{La}, \text{Th})\text{PO}_4$)
- Titanite ($(\text{sphene}, \text{CaTiSiO}_5)$)
- Baddeleyite (ZrO_2)
- Perovskite (CaTiO_3)
- Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$
- Allanite ($\text{Ca}_2(\text{Al}^{3+}, \text{Fe}^{3+}, \text{Fe}^{2+})_3\text{Si}_3\text{O}_{12}[\text{OH}]$)
- Rutile (TiO_2)
- Xenotime (YPO_4)
- Uraninite (UO_2)
- Calcite/aragonite (CaCO_3)
- Thorite ($(\text{Th}, \text{U})\text{SiO}_4$)
- Pyrochlore ($(\text{Na}, \text{Ca})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})$)

Of these minerals only uraninite, thorite, and monazite have $>1\%$ U and/or Th. Minerals most suitable for dating have little or no initial “common” Pb; this means that when dated the Pb contained in the mineral is primarily radiogenic. However, when common Pb is significant, either due to young age or low relative ratio of U/Pb (allanite, apatite, calcite, titanite), minerals can still be dated using an isochron approach, making a correction for the common lead isotope composition. Many of these minerals are amenable to either ID-TIMS or in situ SIMS or LA-ICP-MS dating methods, the latter requiring a reference mineral of the same type for the dating procedure.

Dating of Igneous Events and Related Applications

The early quest in U–Pb geochronology was mainly about determining the age of the Earth. By 1956, sufficient U–Pb ages documented Earth’s age to be >2.6 Ga, and work by Patterson (1956) on meteorite primordial Pb combined with information on terrestrial samples demonstrated that the Earth was ~ 4.5 Ga. Most work in U–Pb geochronology of the 1950s–1960s concerned dating igneous minerals – zircon and titanite – to constrain igneous events and populate the geological time scale and using the punctuated emplacement of felsic volcanic or plutonic rocks to constrain tectonic and orogenic events. These topics are dealt with in other chapters. Zircon became the mineral of choice mainly because it was realized early on that it was very refractory, resisted resetting, and could reveal igneous events in spite of subsequent alteration and metamorphism. Indeed, the work of Gulson and Krogh (1973) and Copeland et al. (1988) documented a phenomenon called “inheritance,” which is the survival (i.e., non-dissolution) of a preexisting phase – zircon and monazite – throughout a melting and magma crystallization event due to saturation of that magma in the mineral in question. These “inherited” grains are used extensively to deduce the age and geochemical characteristics of the source and/or country rock regions of the magmas. Beginning around 1990, the mineral baddeleyite (ZrO_2) began to be dated in diabase and gabbroic rocks by U–Pb methods (Heaman and LeCheminant 1993), allowing reliable and precise ages of mafic magmas, including ophiolites to be dated. This development was paired quickly with palaeomagnetism of such rocks (dyke swarms, major mafic igneous provinces) to more robustly reconstruct the whereabouts of continental fragments dispersed by rifting and to determine the positions of continents on the Earth more accurately throughout geological time. Kimberlite dating by U–Pb is dealt with in a related chapter using the minerals perovskite and baddeleyite. U–Pb

geochronology of igneous zircon and its application to geological problems are addressed in other chapters of this volume.

Meteorite U–Pb Dating

U–Pb geochronology of meteorites is a discipline in itself, requiring very rigorous sample preparation and chemical/isotope measurement procedures; a chapter is devoted to this topic in this volume. The antiquity of meteorites and the rapid change in the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratio early in Earth history resulting from higher $^{235}\text{U}/^{238}\text{U}$ permit very precise dating of crystallization of the earliest materials of the solar system such as chondrules and CAIs (calciumaluminium inclusions). These materials contain relatively high U/Pb ratios, and it has been possible to date these 4,567 Ma old grains to better than ± 0.5 Ma uncertainty.

Earth's Oldest Zircons

In terms of the oldest materials identifiable on the Earth, the detrital zircons of quartzose metasedimentary rocks (Mt Narryer quartzite; Jack Hills conglomerate) of Western Australia have been a gold mine of information. Reasonably abundant ($\sim 3\%$ of detrital zircons) > 3.9 Ga zircons occur in these samples, and they have been dated extensively ($> 100,000$ zircon grains have been analyzed). The geochemical characteristics of these old grains (Hf isotopes, rare earth elements (REE) spectra, oxygen isotopes, Ti thermometry, inclusion mineral characteristics) have been researched at length (Amelin and Ireland 2013); these are mentioned in a related chapter. Among the most interesting conclusions of these studies are that the oldest zircons on Earth are ~ 4.36 Ga, significantly younger than the last stages of crystallization of the lunar magma ocean at ~ 4.42 Ga (Nemchin et al 2009). Hf isotope studies by many authors on these old zircons reveal that most if not all are derived from mantle reservoirs that are depleted to chondritic in composition, indicating that significant silicate mantle differentiation took place very early in Earth history. The extent to which this resulted in “continental” crust, as opposed to mafic crust, is very difficult to determine and no doubt will continue to be a topic of research well into the future. On the basis of existing work, it appears unlikely that zircons > 4.4 Ga will be found on Earth, even though it is certain that scientists will continue to search for them!

U–Pb Dating of Metamorphism and Quantifying Time in P–T Evolution

A related chapter describes the application of U–Th–Pb dating of monazite, xenotime, allanite, rutile, and titanite to the chronology of metamorphism. The chemistry of these accessory minerals makes it a challenge to relate their growth directly to the pressure and temperature conditions of metamorphism, since they do not form directly from reactions of P- and T-sensitive minerals like garnet, aluminosilicates, micas, etc. Nevertheless, studies of Smith and Barreiro (1990) showed how monazite grows in amphibolite facies conditions, appearing usually in the staurolite zone of Barrovian metamorphism, a generalization that still appears to hold. Other minerals such as allanite preserve reaction relationships to apatite and monazite and at times other more abundant rock-forming minerals. Because garnet is a major reservoir for yttrium (Y) and because Y can occur in significant proportions in monazite due to its solid solution with xenotime, Y-zoning is used as a

“monitor” of the presence/relative abundance of garnet during monazite growth. This allows monazite chemistry to be used to relate its growth to conditions of metamorphism defined by other pelitic minerals. Clearly, the textural relationships of these accessory minerals in relation to the fabric of other rock-forming minerals are crucial pieces of evidence concerning the relative age of accessory minerals. For example, inclusions of accessory minerals within other P–T-sensitive phases (garnet, coesite, diamond, etc.) can preserve the oldest prograde metamorphic ages. Phases that grow during decompression and retrogression, for example, titanite in rutile-bearing eclogite, can be used to date the exhumation/retrogression part of the P–T history. In these geological situations, the use of in situ methods is usually a requirement, along with data on mineral chemistry, phase equilibria, textural data, geological setting, and field relations. In situ methods need to measure wherever possible all U–Th–Pb isotopes, not just U–Pb, for monazite, due to the problem of excess ^{206}Pb in Th-rich monazite (Parrish 1990), in order to determine accurate ages in young metamorphic rocks. Often, multiple minerals dated in the same sample will reveal a richer and more complete metamorphic history. A particularly common characteristic, which is increasingly documented in detailed studies of metamorphic rocks, is that monazite growth takes place over a long period of time, including prograde, peak, and in part retrograde conditions. Examples published recently in the Himalaya and in the Cordillera have documented tens of millions of years of time in a rock’s P–T evolution. One of the challenges in doing this in situ work is that reference minerals of well-determined age suitable for age calibration may not exist, prompting the search for better mineral standards, for example, for rutile and allanite (Bracciali et al. 2013).

U–Pb Dates of Minerals as Thermochronometers

Although many minerals datable by U–Pb methods were initially regarded as having high closure temperatures, many of these can be effectively used as thermochronometers. In contrast to zircon and monazite, it has long been documented that the retention of Pb by titanite, allanite, rutile, and apatite is not complete during amphibolite facies conditions of metamorphism or reheating. Early work in case studies showed clearly that U–Pb dates on titanite, rutile, and apatite were generally younger than the peak of metamorphism, often much younger. When considered along with dates from other minerals (micas, hornblende) of known closure temperature, the Pb-retention temperature of these minerals was regarded as being in the range of 400–600 °C. More recent experimental diffusion studies have generally confirmed these estimates. Based on empirical and experimental data, the order of retention of Pb for these minerals from highest retention to lowest is allanite > titanite > apatite > rutile, with allanite and titanite being ~600–650 °C and apatite and rutile being closer to 500 °C. When combined with other thermochronometers (Rb–Sr mica, Ar–Ar hornblende and mica, fission track, U–Th–He), a full thermal history for metamorphic rocks can be established from ~700 °C to <100 °C, with U–Pb dating constraining the thermal and mineral growth history above 400–500 °C (Parrish 2001). Together with chemical and phase equilibria data, the P–t history (exhumation and /or burial) can also be constrained, but to a lesser degree of detail.

Provenance Applications of Detrital Mineral Dating

The identification of the source of clastic sedimentary rocks, or provenance analysis, enables a reconstruction of part of the geological history. The first lines of evidence are clast composition in conglomerate and the composition of grains (lithic, quartz, feldspar, heavy minerals) in sandstone.

However, without further information, few rocks can be proven to be derived from a specific source. U–Pb dating of detrital minerals provides probably the most important information allowing the discrimination of source areas for clastic rocks. Detrital mineral dating began to be tractable once single minerals could be dated. This work began in the mid–late 1980s using single-grain ID-TIMS dating, but the tedious aspect of the dating meant that few grains could be dated in a given study. The appeal of this type of data captured the imagination of geologists, and a new field of research increasingly gained momentum through the 1990s and in recent years. Some of these studies emphasized the desirability of systematically examining the detrital zircon signatures of formations in continents and in orogens, whereas other studies applied this single-grain dating technique to specific problems, for example, the determination of the maximum age of sedimentation of a Precambrian sedimentary rock for which few depositional age constraints existed. This field has exploded into what one might call “mass production” of detrital zircon data, covering most continents’ major sedimentary rock packages and including modern river detritus.

The proliferation since ~2000 of in situ U–Pb dating methods such as LA-Q-ICP-MS has encouraged many geologists to conduct this type of work as “users” who follow a standard, often somewhat unsophisticated, recipe for analysis in order to address provenance questions. This trend involves generating a huge amount of data often illustrated in probability distribution plots that show both uncertainties and abundance of data in only semiquantified form. Sometimes the data are not uniformly rigorously collected, some having no information about whether single zones in zircon are dated, whether data are concordant or nearly so, or whether the $^{206}\text{Pb}/^{238}\text{U}$ or the $^{207}\text{Pb}/^{206}\text{Pb}$ ages are being used for the interpreted age of a grain. Although the data is usually published in supplementary tables online, the interpretation of detailed data is a challenge to obtain as an interested reader. This can compromise the robustness of such datasets. A great variety of quality of data from such studies exists, and this diversity in quality continues to be published. Readers are cautioned to examine data thoroughly and question whether interpretations made are sufficiently rigorous!

Many geological questions pertaining to provenance of sediments simply cannot be answered by zircon single-grain dating alone. Approaches that use the most pertinent geochemical and dating methods are likely to be able to answer questions better, for example, by the use of additional detrital minerals (U–Pb dating of detrital monazite and/or rutile in sediments; Ar–Ar dating of detrital mica) and the use of isotope tracers of dated minerals (Nd in detrital monazite, Sr–Nd in detrital titanite and apatite, Hf isotopes in detrital zircon) (Najman et al. 2008). Excellent science demands a broad approach that is tailored to the question being addressed and which uses the most appropriate isotope methodology.

Sedimentological, Environmental, and Paleoclimate Applications of U–Pb Dating

A chapter on U–Pb applications to diagenetic events is part of this volume and presents methods for addressing this topic. A key part of this field is the application of U–Pb methods (both ID-TIMS and in situ methods) to carbonate (calcite, aragonite) and phosphate that occur as cement or as primary sedimentary materials deposited usually from marine or freshwater (fossils, cements, speleothems, lake carbonate, carbonate veins, hominin or other animal phosphate). While there are currently few extensive studies published, it is clear that this is a field that will grow rapidly in the near future.

U is partitioned into aragonite in marine fossils, and calcite includes sufficient U to also be dated, when the initial incorporation of lead into the mineral is low, as is often the case with precipitation of calcite from groundwater. Thus when a material has a high U/Pb ratio, these carbonate or phosphate minerals can be dated, by either ID-TIMS methods (Smith and Farquhar 1989; Rasbury et al. 1997; Richards et al. 1998) or by a combination of ID-TIMS and in situ methods (Woodhead et al. 2012). Indeed it is now tractable to apply LA-ICP-MS using high-sensitivity instrumentation to date calcite in situ even when the U content is not particularly high, via the use of a calcite standard. This field of research will likely explode in popularity and demand over the next 10 years.

Collaboration and Improvement of Methods

The field of U–Pb dating has come a long way since its inception by the work of Boltwood and Holmes about 100 years ago in the period immediately following the discovery of radioactivity. With the development of sufficiently sensitive mass spectrometry by Nier in the 1930–1940s and the availability of isotope tracers of U and Pb in the 1950s and 1960s, the field of ID-TIMS exploded with refinement of methods, use of Teflon acid distillation and mineral dissolution vessels and multi-collector high-sensitivity mass spectrometers. Recognition of complex zircon growth histories demanded the development of better ways to analyze concordant zircons and develop in situ methods, which in the past 20 years have exploded in availability and popularity. This has brought U–Pb geochronology within reach to geologists, some of whom never worked in a laboratory previously. Nevertheless, the advancement in methods is very impressive, both intellectually and technologically. Innovative applications of U–Pb dating to geological problems have generally kept pace with technology, because geological questions usually precede the availability of efficient and accurate instrumentation and methods. For example, widespread detrital single-grain dating had to wait until efficient in situ methods of analysis of large numbers of grains became available. The use of single grain rutile U–Pb dating in provenance studies will become more common following the recent development of rutile reference materials and sensitive LA-ICP-MS methods (Bracciali et al. 2013). Similarly, the availability of calcite U–Pb reference materials and sensitive mass spectrometry capable of measuring young ages precisely in minerals with low U contents is just now tractable; this will cause a rapid increase in demand and application of U–Pb dating to calcite and Quaternary materials, hardly addressed at the present time.

Collaboration among U–Pb laboratories has been essential because of the inherent ability of ID-TIMS methods to measure isotope ratios apparently more precisely than one can confidently calibrate isotope tracer solutions. The EARTHTIME project (www.earth-time.org) is one of these international efforts that has recognized the need for more collaboration and use of common solutions to monitor and measure interlaboratory data, to ensure that it is comparable, and to encourage laboratories to quote uncertainties that are accurate and realistic. For example, age solutions and mixed ^{233}U – ^{235}U – ^{205}Pb isotope tracers are available to world laboratories for the purpose of improving the precision and accuracy of data produced. This effort has been extended, for example, to U-series dating and to in situ methods of U–Pb dating, so that numerous world laboratories are able to compare data, assess their own performance against international standards, and share the best practice. This type of collaborative philosophy, combined with continued technological and method innovation, is the way forward for this important area of geochronology.

Q5

Cross-References

- ▶ Geological Time Scale
- ▶ Laser Ablation Inductively Coupled Mass Spectrometer (LA ICP-MS)
- ▶ Mass Spectrometry
- ▶ Radiation and Radioactivity
- ▶ Secondary Ion Mass Spectrometer (SIMS)
- ▶ Tectonic Processes (Thermochronology)
- ▶ Thermal Ionization Mass Spectrometer (TIMS)
- ▶ U-Series Dating
- ▶ Uranium–Lead, Chemical Isochron U–Pb Method (CHIME)
- ▶ Uranium–Lead, Dating
- ▶ Uranium–Lead, Detrital Zircon
- ▶ Uranium–Lead, Hydrothermal Events
- ▶ Uranium–Lead, Igneous Rocks
- ▶ Uranium–Lead, Metamorphic Rocks
- ▶ U–Th:He Dating

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Luminescence Dating, Meteorites

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Thermoluminescence is the light produced as a result of heating. In crystalline silicate rocks, there are a variety of possible energy levels at which electrons can reside, such as the valence band and the conduction band. Ionizing radiation passing through the crystals can transfer to the electrons sufficient energy to promote them from the valence band to the conduction band where they freely move through the crystal lattice. If they locate “traps,” they can remain at an elevated energy level. Traps are typically lattice defects or impurity ions, an important example being Mn^{2+} substituting for Ca^{2+} in a silicate lattice. Calcium is an abundant element, and Ca-bearing minerals are common in meteorites, most notably as the mineral plagioclase, a Ca aluminosilicate. The traps are typically an electron volt or so below the conduction band, and this energy has to be supplied to release them. One means of supplying the required energy is by heating the crystal. Once released, the excited electrons can find their way to the ground state by way of a “luminescence center” when their excitation energy is released as a photon, normally in the visible range. The number of excited electrons determines the intensity of light emitted, and the temperature at which it is emitted, as the crystal is heated, is determined by the depth of the trap below the conduction band. Deeper traps require higher heating temperatures. Being a solid-state property, there is a distribution of traps about some mean value, and the release of electrons from traps is governed by a probability function, e.g., the Arrhenius equation, so TL peaks are fairly broad. In addition, there are usually many kinds of trap in a typical crystal lattice, so there are multiple overlapping peaks in a typical experiment. The data are recorded as light emitted as a function of heating temperature, and the resulting plot is called the “glow curve.”

Meteorites have a wide variety of composition and mineralogy, but plagioclase is present in most of them and gives rise to their thermoluminescence. There are a few exceptions, in which plagioclase is absent and the thermoluminescence is produced by pyroxene, an Mg silicate. Pyroxene has at least two types of trap, one being Mn^{2+} substituting for Mg^{2+} , but pyroxene luminescence is “quenched” (destroyed) in the presence of Fe^{2+} which provides pathways for the electrons to reach the ground state without a visible transition. A recent review of the application of thermoluminescence to the studies of extraterrestrial materials is given by Sears et al. (2013).

The thermoluminescence mechanism enables several potential means of dating a meteorite. An early idea was that the traps were dislocations caused by radiation damage so that the number of traps built up with time and thus provided a “clock.” The basis of the idea was an observed correlation between induced TL and potassium-argon age (Komovsky 1961). Induced TL (sometimes referred to as “artificial TL” in the early literature) is the TL signal obtained by draining the meteorite of its natural TL and exposing the meteorite to a standard test dose of radiation in the laboratory. The idea of induced TL as a clock has not withstood the test of time, however, since exposure to radiation doses and fluencies greater than the meteorite experienced in nature do not change the induced TL response (Sears 1980). Instead, it seems that meteorites with low induced

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TL and too young potassium-argon ages have experienced severe shock-heating events that melted the plagioclase and caused the loss of Ar. Thus, while induced TL failed as a proposed chronometer, it succeeded as a new means of evaluating the shock-heating history of meteorites.

Thermoluminescence dating applications that have been proposed and developed in the literature and that have some degree of success are as follows.

Terrestrial Age Determination by TL Fading. Terrestrial age determination for meteorites, the time that has lapsed since their fall from space, has taken on particular interest with the discovery of large numbers of meteorites in the prairies, deserts, and Antarctic ice fields. A meteorite in space is exposed to large doses of radiation from internal radioactivities and cosmic rays, cosmic rays being the more important in the short term. The level of TL is determined by a competition between decay at ambient temperatures and buildup depending on the radiation dose rate. Once on Earth, the meteorite is shielded from the high dose of cosmic rays experienced in space and stored at a higher temperature on Earth than in space, so the TL level adjusts to the new environment by slowly fading to its new lower equilibrium level. Thus, one has the potential to determine how long the meteorite has been on Earth from the extent of fading. There are two issues to be resolved. One is that meteorites enter the atmosphere with a wide variety of natural TL levels, depending on the temperature of the object in space and the degree of “shielding” available to the sample, that is, how deeply it was buried within a larger body while in space. There is no way around this problem, and shielding is a problem shared with the isotopic methods for determining terrestrial age such as those using the decay of radiocarbon. The second issue is the effect of different storage temperatures on Earth, but these can be handled fairly well from knowledge of climate temperatures and theoretical modeling of the decay process. Several major studies of this process have been reported (Melcher 1981; Sears and Durrani 1980; Benoit et al. 1991; Sears et al. 2011), and it was one reason for routine natural TL measurements being incorporated in the US Antarctic Meteorite Program (Hasan et al. 1987).

Terrestrial Age by Buildup of TL in the Meteorite Just Under the Fusion Crust. This is sometimes referred to, somewhat misleadingly, as “fusion crust dating.” As a meteorite passes through the atmosphere, its surface is heated to the extent that a conspicuous melt crust is formed. The high heat capacities of silicate rocks and the ability of the melt to flow away from the meteorite mean that the heat of atmospheric entry does not penetrate far into the meteorite. However, for a few millimeters under the fusion crust, the meteorite will have been heated enough to drain the natural TL. Once on Earth, environmental radiations will cause the TL to build up again, and there is the potential to determine terrestrial ages using the same methods as used for dating pottery. The level of TL is measured and converted into an absorbed dose using laboratory calibration experiments. Then, the environmental radiation dose rate is determined by placing dosimeters in the field. Finally, absorbed dose is divided by dose rate to determine the age. Only a few studies have been made of this technique, but the results seem promising (Miono and Nakanishi 1994; Akridge et al. 2000).

Cosmic Ray Exposure Age by Natural TL Buildup. There has always been a sense that the thermoluminescence phenomenon should yield a means of determining cosmic ray exposure age, literally the time that has lapsed since the meteorite became exposed to cosmic rays. Consistent with this idea is the observation that the natural TL levels observed throughout large pieces of meteorite vary, reflecting the buildup and decay of primary and secondary radiations during cosmic ray exposure. However, it is only recently that quantitative efforts have been made (Biswas et al. 2011) in this direction, and the technique is in its infancy.

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Luminescence, Soils

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Definition

Luminescence dating measures the time since quartz and feldspar mineral grains were last exposed to light. Dating soils with this method quantify the last time mineral grains sampled from within soil profiles were at the ground surface.

Soils can be defined in many different ways depending on the environmental context. For the purposes of this application, soils are defined as colluvial material produced from underlying parent material and being transported by various physical processes. Windblown soils, agricultural soils, and deep chemical weathering profiles are not considered here.

Introduction

Hilly upland landscapes are cloaked in a thin layer of soil derived primarily from the underlying parent material (Carson and Kirkby 1972; Dietrich et al. 1995; Heimsath et al. 1997) (Fig. 1). Understanding how the Earth's surface evolves under changing climatic, tectonic, or human land-use forces thus includes understanding how these physically mobile upland soils are produced and transported. Setting aside landslides, which are likely to dominate soil erosion in steep and mountainous terrain, soil moves slowly downhill by creep and slope wash. Observations from gently rounded hills show that soil thickness increases with distance downslope, supporting the view that creep occurs by diffusion-like processes with the amount of soil moving being linearly proportional to surface slope (Carson and Kirkby 1972; Heimsath et al. 1999; Young 1960). Such movement of individual soil grains could be caused by burrowing creatures (worms, ants, gophers, etc.) and by tree throw (trees uprooted, typically by high winds, often carry soil and bedrock attached to the root wad) coupled with localized slope wash. Field observations and laboratory studies also show that other processes may also transport the soil, including shear and depth-dependent viscous-like flow (Carson and Kirkby 1972; Fleming and Johnson 1975; Selby 1993; Young 1960). Tracking the transport paths of soil particles helps build our understanding of these processes (Fig. 2). Dating the last time soil minerals were at the ground surface can enable further quantification and establishing mathematical relationships capturing the essence of these processes. These relationships can then be used in models that can help predict soil sustainability, landslide frequency, and magnitude and also help develop water management and land-use development plans.

Other Methods for Dating Soils

Early thinking about how hilly, upland landscapes evolve with time recognized that landscape morphology likely reflects the long-term dominant process shaping the landscape (Davis 1892;

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Fig. 1 (a) Photograph of typical soil-mantled hillslope used for studies such as the ones covered in this chapter. This one is from Point Reyes, CA, during the late summer dry season. (b) Photograph of the well-mixed colluvial soil that mantles the same landscape enriched with organic matter and quite moist during the winter rains. Note the well-defined boundary between the physically mobile soil above (*dark layer*) and the underlying weathered bedrock that retains relict rock structure and is considered to be in place. *Holes* are from bulk density sampling

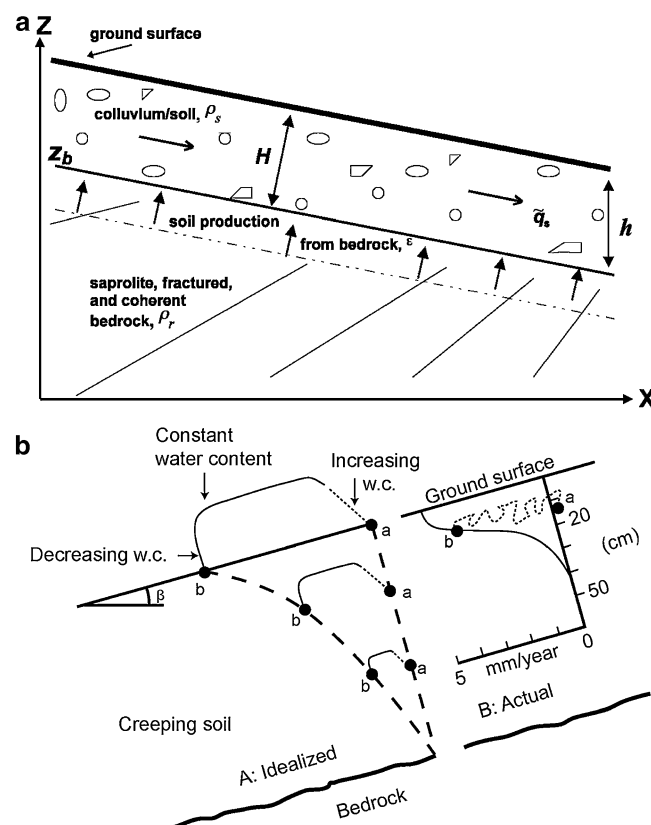


Fig. 2 (*Upper Panel*): The conceptual framework as used by Heimsath et al. (1997) and similar studies for vertical soil depth, h indicating that the slope-normal depth, H , is equal to the vertical depth times the secant of the slope angle. The change in soil mass in a column of soil with time is equal to the production of soil from the underlying bedrock minus the balance of soil transported past the column. (*Lower Panel*): Idealized displacement profile (a) showing how soil particles might move from a to b in a “laminar flow” path envisioned by Fleming and Johnson (1975) and later sketched in by Selby (1993). The *right-hand side* (b) shows Selby’s sketch of the commonly recognized “chaotic” flow path of soil particles that may be mixed while the soil profile is shrinking and swelling from changing water content

Gilbert 1909). Specifically, the observation that smooth hillslopes tended to steepen with increasing distance from the drainage divide led to the assumption that sediment transport flux, which must increase with increasing distance from the divide, is proportional to topographic gradient. This led to the writing of a linear transport relationship, which became known as the “diffusion equation” because of its similar form to Fick’s law of heat diffusion. Because creep processes were thought responsible for transport that could be modeled as “diffusive,” the term “diffusion” became synonymous with creep. Recently, more accurate terms such as “diffusion-like” or “linear transport relationship” are favored since soil particles are not actually diffusing downhill. They are, however, moving in a creep-like way as gravitational force imparts a downslope preference to any physical disruption of the soil. Quantifying the process necessitates dating or tracking the particles.

Physical Tracers

An innovative and not often repeated study attempting to quantify soil movement using physical tracers was published in *Nature* over half a century ago (Young 1960). The study recognized the importance of quantifying rates and processes of hillslope denudation and set about doing it by initially inserting metal pegs into the ground surface at regular intervals downhill from a bedrock outcrop, noting the distances carefully and tracking surface movement of clasts over time. The uncertainty involved with peg surface displacement was huge, and the problem with discerning surface transport from downslope movement occurring within the soil profile led to a modification of the method to develop what became known as a “Young Pit.” Despite two publications in *Nature* (Young 1960, 1963a), few studies have followed the lead of this challenge (e.g., (Finlayson 1981; Schumm 1967), including a modified approach (Richards and Humphreys 2010) that yielded results no less equivocal. Even the results of Schumm (1967), often cited as one of the few field-based studies quantifying soil transport processes, show considerable scatter and were collected over a 7-year period, longer than most are willing to devote to a single study. Given the results (or lack thereof) from the two most recent studies (Clarke et al. 1999; Richards and Humphreys 2010), few others have attempted to follow Andrew Young’s inspirational lead.

Tephra Deposits

Fortunately, geochemical methodological advances have enabled us to directly quantify processes and rates with significantly less uncertainty and physical effort. Another innovative approach that involves using a physical tracer that does not involve human disturbance (i.e., the digging of numerous Young Pits) is worth summarizing. Of course, this physical tracer method also involves using geochemistry, as the studies do rely on relatively precise geochemical dating (using calibrated ^{14}C dating) of tephra deposits in upland soils. Two recent studies documented profiles of tephra concentrations in hillslope soils and combined a detailed mapping of these concentrations with topographic derivatives to quantify soil transport processes (Roering et al. 2002; Walther et al. 2009). In both cases, one on a series of incised fluvial terraces along the Charwell River, South Island, New Zealand (Roering et al. 2002), and the other along a hillslope transect in the Blue Mountains, SE Washington state, USA (Walther et al. 2009), the tephra deposits are well dated and are treated as marker beds in the hillslope soils. Both studies involved extensive sampling of soil pits and auger profiles to quantify tephra distributions in the hillslope soils. Because the sample locations were located along profiles characterized by the topographic properties supporting linear transport relationships, the topographic derivatives were used with tephra distribution and concentration to provide calibrated transport relationships for each field site. Given the paucity of such field-based data supporting transport relationships, these studies are especially important. Given how difficult it

is to find such ideal field locations where there are both well-dated tephtras and hillslopes of characteristic form, such an innovative method is unlikely to be broadly used.

Short-Lived Isotopes (^{210}Pb and ^{137}Cs)

A technically less cumbersome approach involves using short-lived isotopes measured in bulk soil samples that can be collected without any disruption (i.e., by inserting tracers) and without any special site characteristics (i.e., dated tephtra layers). These fallout-derived radionuclides are used extensively in erosion and sediment transport studies on both agricultural and forested landscapes. Atmospherically delivered ^{210}Pb and weapons-derived ^{137}Cs can be used alone or simultaneously to quantify and trace erosional processes (Wallbrink and Murray 1996; Walling and He 1999a, b; Whiting et al. 2001). Relative rates of soil mixing can be evaluated through measurements of nuclide activities in soil profiles (Dixon et al. 2009; Dorr 1995; Kaste et al. 2007; Tyler et al. 2001). Because these isotopes are deposited at the soil surface, mixing processes can increase the dispersion of nuclides with depth and the overall downward transport rate. For example, on agricultural landscapes, where tilling homogenizes the soil to the depth of the plow layer, a unique, well-mixed ^{137}Cs profile captures the process (Walling and He 1999a). By measuring the vertical distribution of fallout radionuclides in soils and calculating diffusion-like coefficients, the sediment transport mechanisms and mixing rates are quantified over 10- to 100-year timescales.

Meteoric ^{10}Be

In addition to short-lived isotopes, fallout-delivered (or garden variety) ^{10}Be can be used to quantify hillslope sediment transport processes over longer timescales (Jungers et al. 2009; McKean et al. 1993; Monaghan et al. 1983). Meteoric ^{10}Be is a cosmogenic radionuclide well suited for use as a tracer of soil movement over geomorphic timescales. Spallation of oxygen and nitrogen in Earth's atmosphere produces the majority of ^{10}Be present in natural systems (Lal and Peters 1967). Following production, ^{10}Be is delivered to the Earth's surface at a rate most significantly proportional to regional precipitation fluxes. A smaller, but not insignificant, inventory of ^{10}Be falls from the atmosphere adsorbed to terrestrial dust. The timescale over which any radioactive tracer is useful is a function of the rate at which the isotope is produced and/or delivered to the natural system of interest and of the rate at which the radionuclide decays (^{10}Be has a half-life of 1.39×10^6 years) making it especially useful as a tool for quantifying rates of Earth surface processes that take place over thousands to millions of years. Additionally, ^{10}Be adsorbs quickly and strongly to soil particles and a soil mantle's total ^{10}Be inventory can reliably be accounted for if samples integrate from the soil-atmosphere interface to the contact between soil/saprolite and unweathered bedrock. Naturally, it follows that landscapes with relatively thin (0–150 cm) soil mantles are best suited to the task of capturing complete ^{10}Be inventories. Measurement of meteoric ^{10}Be is not trivial or inexpensive, however, and application of this methodology is limited.

Luminescence Dating of Soils

Rods, blocks, and flexible tubes inserted in the soil are too clumsy to examine grain scale sediment transport, which requires the use of labeled particles (Selby 1993). Insertion and detection of labeled grains throughout a soil mantle with microscale positional measurements would be a massive undertaking (Cox 1990; Cox and Allen 1987; Nichols 2004). Assuming, however, that grains brought to the surface by bioturbation and tree throw are buried again, vertical mixing at the grain scale may be determined by measuring the time since individual soil grains last visited the surface.

This was first done by single-grain optical dating, which is based on an optically stimulated luminescence (OSL) signal that accumulates within buried quartz grains and is reset to zero by exposure to sunlight (Heimsath et al. 2002).

OSL became the established successor to thermoluminescence (TL) as the means for measuring the time elapsed since a mineral grain's last exposure to sunlight (e.g., Aitken 1985; Aitken 1994; Duller 1996; Huntley et al. 1985; Roberts et al. 1990; Roberts et al. 1997). The OSL measurements from quartz and feldspar grains focus on the most light-sensitive electron traps, less readily measurable than TL. While exposure ages can be measured from both minerals, quartz is the dosimeter of choice because the microdosimetry in feldspar grains is complex and the stored dose decays unpredictably (Murray et al. 1995). The OSL dating initially used gram-sized samples of thousands of sand grains. The second stage of development involved the "small aliquot" methods, which used a few tens to a few hundred mineral grains per sample. Several recent reviews provide details of the methodology (Fuchs and Lang 2009; Madsen and Murray 2009; Rhodes 2011; Stockmann et al. 2013). The essence of the methodology applied to dating soils involves following detailed steps that are expanded upon in the above references.

While most applications of OSL dating of soils have been toward dating human artifacts and sedimentary deposits, the methodology can readily be used to quantify hillslope sediment transport rates and to distinguish between different transport processes. Optical ages of grains from different depths depend on transport processes: for example, grains moving in a surface layer would intermittently be exposed to sunlight, whereas grains never exposed at the surface should show "infinite" ages. Alternatively, mixing throughout the entire soil column would lead to finite-aged grains from the soil surface to its base, the boundary with the underlying saprolite, and the source of the mobile soil.

Downhill movement of any soil grain resolves into slope-normal and slope-parallel components. Only the slope-normal velocity of a grain can be derived from its optical age. Such methods cannot assess the slope-parallel velocity of individual grains, but the depth-averaged velocity can be calculated if the rate of soil production from rock weathering is known at all points and if the topography of the site is well constrained. Soil-production rates were previously determined from measurements of the in situ cosmogenic nuclides ^{10}Be and ^{26}Al (Heimsath et al. 2000) and were then used in a new way by Heimsath et al. (2002) to derive slope-parallel velocities. Additionally, modeling of the landscape evolution of the site (Braun et al. 2001) highlighted the need for more detailed field understanding of sediment transport processes active on soil-mantled landscapes. Unfortunately, the resource intensity of using OSL to date individual soil grains and attempt to fully quantify soil transport processes proves to be a significant hurdle.

More recent work expanded upon the methodology of Heimsath et al. (2002) by using OSL to derive soil-mixing rates for a set of soil pits from hilltop to base (Stockmann et al. 2013). Similar results led the authors to discern between soil grains that had been mixed throughout the soil column, ones that had never been to the surface and ones that were very recently bleached by the sun. The authors did not use the ages to determine or verify a transport relationship for the sediment transport at the site, but were able to quantify mixing rates and suggest that faunal mixing was less dominant than at other studied sites.

Summary and Conclusions

Establishing chronologies for profiles of soils and for young sedimentary deposits is an essential aspect of quantifying sediment transport processes and rates. Dating soils also enjoys wide

application to archaeology, land-use management, tectonic geology, and sedimentary geology. It is, however, exceedingly difficult to do and decades of work involving scores of researchers and a wide variety of methodologies have been devoted to it. Luminescence dating, specifically OSL and especially single-grain OSL, shows great promise as the leading methodology that enables both an accurate and precise dating tool that is ideally suited to the task. There are, however, essentially only two studies that have applied single-grain OSL dating to the rich problem of dating soils and using the dates to better understand erosional processes. The other applications of dating soils (sediments) have focused on the age of the deposit for archaeological needs rather than geomorphic. There are many challenges to overcome before this methodology becomes more widespread. First and foremost is the fact that sample collection is challenging and needs to be carefully tailored to the process geomorphology of the site in question. Second and related to the first because of the limits on sample numbers is that the method is relatively expensive, with each analysis approaching the cost of obtaining a cosmogenic nuclide age analysis. Third, there remain sources of significant uncertainty in establishing the particle flow paths such that interpreting the OSL age can be a challenge. Given the nearly endless list of exciting scientific problems that can be tackled using luminescence dating of soils, it is likely that these challenges will soon be overcome and this method will truly shine.

Cross-References

- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating of Archaeological Sediments](#)
- ▶ [Luminescence Dating, Dose Rate](#)
- ▶ [Luminescence Dating, History](#)
- ▶ [Luminescence Dating, Instrumentation](#)
- ▶ [Luminescence Dating, Single Grain Dose Distribution](#)
- ▶ [Luminescence, Colluvial Sediments](#)
- ▶ [Luminescence, Geomorphological Processes](#)

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Luminescence Dating, Uncertainties, and Age Range

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Definition

Luminescence ages have an uncertainty of at least 4–5 %, mainly due to systematic errors in both dose rate (conversion factors) and equivalent dose (source calibration) estimation. In most cases, the uncertainty will be higher, due to random errors (e.g., spread in equivalent doses) or uncertainty in assumptions (e.g., water content fluctuations, burial history). Dating is possible for a wide age range of a few decades to about half a million years, although uncertainties are usually relatively large toward the extremes of this range.

Uncertainties

As with any method, results of luminescence dating contain errors or uncertainties. Adequate assessment of errors is important, for instance, to correctly assess rates of processes or leads and lags in natural or anthropogenic systems, or contemporaneity of different sites (e.g., Guerin et al. 2013). It is common practice in the luminescence community to present 1-sigma uncertainties, implying that there is a 68 % likelihood that the true answer is within the presented range. This of course only holds if all sources of uncertainty are adequately considered.

Error propagation in luminescence dating is not straightforward. Uncertainties in both dose rate and palaeodose estimation should be taken into account, as both contribute equally to the uncertainty in the final age estimate. Moreover, the errors should not only comprise the measurement uncertainties (e.g., counting statistics) but also the uncertainties in instrument calibration and parameters used in calculations. Finally, difficult-to-quantify errors may arise from assumptions made for equivalent dose or dose rate calculation. The most-important sources of uncertainty are discussed below, differentiating between random and systematic errors. The first arise mainly from counting statistics and may be reduced by additional measurements (i.e., longer duration, more samples, larger samples). The latter are usually related to instrument calibration, conversion factors used, or assumptions made and cannot easily be reduced.

Equivalent Dose Uncertainty

Statistical aspects of equivalent dose estimation have recently been discussed in detail by Galbraith and Roberts (2012). Here we provide a short summary of the most relevant information:

Individual Aliquots

Luminescence measurements for luminescence dating are carried out on subsamples; each of these aliquots consists of a single grain or a group of grains (up to many thousands for fine-grained dating).

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In the widely used single-aliquot regenerative dose (SAR) procedure for equivalent dose determination (Murray and Wintle 2000, 2003; Wallinga et al. 2000), repeated luminescence measurements are made on the same sample, to compare the natural luminescence signal to artificially induced signals and to monitor and correct for luminescence sensitivity changes during this procedure. For each of the luminescence measurements, the true luminescence signal is estimated based on the measured value. The uncertainty in the estimate is a function of the brightness of the signal and that of the associated background signal that is subtracted to obtain a net signal (Poisson statistics assumed). The uncertainty in the equivalent dose estimate of the aliquot should take the uncertainties in each of these individual estimates into account, as well as the uncertainties in fitting a dose–response curve through the data (see Duller 2007; Galbraith and Roberts 2012), and the additional error arising from instrumental uncertainty (e.g., Duller 2007).

Sample

In the next step, data obtained on the aliquots is combined to obtain the best estimate for the equivalent dose of the sample. For an ideal dataset showing a normal distribution around the mean and identical error terms, this can be done using the mean and standard error on the mean. Here the standard error (standard deviation divided by the square root of the number of measured aliquots) is used, as we are interested in how well we know the mean value. For estimates with widely differing uncertainties, it may be beneficial to use a weighted mean, where the best known estimates are given more importance than the lesser known points. However, use of the weighted mean assumes that there is a true burial dose to which all grains/aliquots belong, and the departure of the measured data from this value is due to the known uncertainties of measurement (i.e., the error term). In the real world this is not the case – even if the measurement uncertainties were infinitely small, the equivalent doses would not be identical.

The Central Age Model (CAM) (Galbraith et al. 1999) provides a better estimate of the burial dose. The CAM presumes instead that the single-aliquot equivalent doses are drawn from a log-normal distribution; the parameters of the distribution are then the “central age” (=burial dose) and the “overdispersion” (the relative standard deviation of the underlying log-normal distribution) and are determined by iteration or optimization. There is a straightforward estimate of the uncertainty on both parameters implemented in the model.

For datasets affected by heterogeneous bleaching, the true age is not represented by the mean or weighted mean, but is more likely to be at the lower end of the equivalent dose distribution. The correct estimate may be found using methods that distinguish dispersion in the data due to heterogeneous bleaching and dispersion from other sources. The Minimum Age Model (Galbraith et al. 1999) is most widely applied, although an alternative approach has been proposed by Thomsen et al. (2007); a study on young floodplain deposits from Australia yielded similar results for both methods (Sim et al. 2014). A crucial aspect in interpreting equivalent dose distributions is to quantify the spread due to sources other than heterogeneous bleaching. Such spread firstly comes from counting statistics, but this error can be adequately quantified and taken into account; it does not contribute to the overdispersion (Galbraith and Roberts 2012). There are two categories of overdispersion: (1) Intrinsic sources are the effect of experimental limitations and can be quantified using dose recovery experiments on uniformly gamma-dosed samples (Thomsen et al. 2007). (2) Extrinsic sources reflect true variation in burial doses, e.g., due to beta dose rate heterogeneity (e.g., Cunningham et al. 2012). Both sources should be quantified to accurately interpret equivalent dose distributions.

Arnold and Roberts (2009) report that 20 % overdispersion is typical at single-grain level for well-bleached samples, and Cunningham et al. (2011a) discuss how this value changes with aliquot size.

However, both intrinsic and extrinsic sources of scatter are likely to vary between samples (Arnold and Roberts 2009) and with absorbed dose (Thomsen et al. 2007, 2012). For this reason, it is advisable to include an uncertainty in the assumed overdispersion when adopting the Minimum Age Model. Such an approach has been proposed by Cunningham and Wallinga (2012); their bootstrapping approach provides reasonable uncertainty estimates for heterogeneously bleached samples, by linking uncertainty to the number of aliquots consistent with the minimum dose/age.

Calibration

The random errors in equivalent dose based on measurement uncertainties and spread in distribution may in principle be reduced by enlarging the dataset or improving the measurements. For the final error estimate, these sources of error should be combined with the systematic uncertainty in calibration of the radioactive source used for equivalent dose determination. Bos et al. (2006) have described a detailed calibration procedure and argued that the uncertainty in calibration is at least 2 %.

Other Errors

The premise of luminescence dating methods is that the dose–response of the natural luminescence signal can be reconstructed in the laboratory, allowing the burial dose to be inferred. Protocols like the SAR accomplish this by taking shortcuts: using preheats to simulate the effect of time on the OSL traps and high laboratory dose rates to simulate the low dose rates in nature. Subtle imperfections in this methodology can induce error in the equivalent dose. For example, the OSL signal may be sensitive to the rate at which the radiation dose is given, contributing to the poorer accuracy observed for older samples (Bailey 2004); the signal is also sensitive to the choice of preheat used (Wintle and Murray 2006). These sources of error are usually ignored, likely because it is very difficult to quantify the uncertainties associated with them. As a consequence, the errors are not reflected in the quoted uncertainty, but rather they define the practical limits of OSL dating. Anomalous fading of the feldspar signal also falls into this category of error; corrections for anomalous fading are sometimes made, but uncertainties associated with such corrections may be large and nevertheless are rarely addressed explicitly (e.g., Kars et al. 2012).

Total Equivalent Dose Uncertainty

For ideal samples, the total uncertainty in equivalent dose is dominated by the uncertainty in the calibration of the beta source and can be as small as 2 %. Measurement of limited number of subsamples and/or scattered equivalent dose distributions may lead to larger errors.

Dose Rate Uncertainty

Concentration Measurements

As with the equivalent dose estimate, there are multiple sources of error in the dose rate estimation. The sources of error depend on the method used for dose rate determination. Usually radionuclide concentrations are estimated either by measuring activity concentrations (e.g., gamma spectrometry) or by estimating radionuclide concentrations based on measured chemical concentrations (e.g., ICP, neutron activation analysis). The quoted errors should include both the random (counting statistics) and systematic (instrument calibration) errors. Minimal feasible relative errors are about 3 % (Murray and Olley 2002).

Conversion Factors

In the second step, infinite matrix dose rates are calculated from the radionuclide (activity) concentrations using conversion factors (Guerin et al. 2011). Unfortunately, neither Guerin et al. (2011) nor previous publications on this topic (e.g., Adamiec and Aitken 1998) discuss uncertainties in the conversion factors. Murray and Olley (2002) estimated an uncertainty of 3 % on the conversion factors, a value that is still reasonable for the updated conversion factors (Guerin, pers. com.).

Attenuation Factors

The third step involves the conversion of infinite matrix dose rate to dose rates in the grains of interest. This dose depends on the grain size due to partial shielding of the inside of the grains to beta irradiation. This effect, combined with effects of etching the surface of quartz grains during sample preparation, is taken into account in the beta attenuation factor (Brennan 2003). The uncertainty in beta attenuation factor is usually assumed to be around 2 % (Murray and Olley 2002). Then, the shielding effect of water should be considered (Aitken 1998), where 1 % by weight of water decreases the dose rate by about 1 %. Any uncertainty on the time-integrated average water content should be reflected in uncertainty in the water attenuation factor and hence the dose rate. Uncertainties in dose rate due to water content errors can be minor (<3 %) for sandy deposits, especially when the water content history is well established, e.g., because it is clear that the sampled material has always been above or below the groundwater table. However, for clay-rich sediments which can double in weight due to water uptake, uncertainties in dose rate due to poorly known water content history can be huge (>100 %). This is particularly relevant to lake-bed sediment, where water content can also change over time due to sediment compaction (e.g., Buylaert et al. 2013)

Cosmic Rays and Alpha Particles

Finally, the contribution of cosmic rays and internal alpha particles to the total dose rate should be considered. The cosmic dose contribution is well defined based on geographic location, height, and burial given by the present-day burial depth (Prescott and Hutton 1994; Madsen et al. 2005). However, in many cases, the burial history is not well established, leading to a relative uncertainty of about 10 % in the cosmic dose contribution. In most cases, the cosmic dose rate is a small portion of the total dose rate, and uncertainties will have a minor impact on overall uncertainties (<2 %). However, in exceptional cases of shallow deposits with low radionuclide concentrations (e.g., quartz-rich deposits), the cosmic dose may contribute up to 50 % of the total dose rate (e.g., Rink and Lopez 2010). The internal alpha dose is usually estimated based on literature information (e.g., Vandenberghe et al. 2008). Although the relative uncertainty in internal alpha dose is large (up to 50 %), the effect on total dose rate is usually limited (<2 %) due to the small relative contribution to the total dose rate.

Other Sources

In addition to the sources of error discussed above, additional uncertainties may arise for specific cases. When feldspar minerals are used, the dose rate should include the contribution from internal potassium and rubidium. Usually, concentration of these radionuclides is not known for the measured grains, and a standard value and uncertainty is assumed (Huntley and Baril 1997; Huntley and Hancock 2001). For fine-grained material, or non-etched grains, the external alpha contribution should be considered and require adequate assessment of the alpha dose and alpha efficiency as well as their associated uncertainties. Also, disequilibrium in decay chains may add to the uncertainty in the final dose rate (e.g., Olley et al. 1997).

Total Dose Rate Uncertainty

For ideal samples, the uncertainty in dose rate is dominated by uncertainties in radionuclide (activity) concentrations (3 %) and conversion factors (3 %). The combined effect of these is around 4 %, which is considered the minimum reasonably attainable uncertainty on dose rate. In many cases, uncertainty will be greater due to uncertainties in burial history and water content. Uncertainties mostly vary between 5 % and 10 % for suitable and less-suitable circumstances, respectively.

The calculation of dose rates and their uncertainties described above make two key assumptions. The first is the “infinite matrix” (IM) assumption, in which the radiation emitted from the sample is equal to that coming in from the surroundings. The second is the “uniform matrix” assumption, in which all parts of the sample are identical. When these assumptions are broken, a correction must be made, implying an increase in the total uncertainty. For example, an object or sedimentary bed within 20 cm of the sample may break the IM assumption (e.g., Wallinga and Bos 2010) as will be the case for deposits that remained at shallow depth for part of their burial history (e.g., Madsen et al. 2005); an irregular sample component, such as shells or pebbles, may break the UM assumption (Cunningham et al. 2011b).

Age Uncertainty

Simple error propagation is usually applied to obtain the uncertainty on the age estimate from uncertainties in equivalent dose and dose rate. Based on the minimal feasible uncertainties presented above, an error of 4–5 % of the age could be obtained (e.g., Ballarini et al. 2003; Roberts and Plater 2007). Smaller uncertainties are not realistic, larger uncertainties are the norm due to limited and/or scattered equivalent dose datasets, and uncertainties in burial history and time-averaged water content.

For larger datasets, uncertainties may be reduced by combining results from a single event layer or by incorporating prior information (e.g., the stratigraphic order) into a Bayesian framework (Rhodes et al. 2003; Cunningham and Wallinga 2012). Care should be taken to differentiate between random and systematic errors. When analyzing the internal consistency of a dataset, only random errors need to be included. However, when luminescence ages are combined or compared with other age information, the systematic errors should also be considered. This issue is discussed in detail by Rhodes et al. (2003).

Age Range

Luminescence dating is a family of methods, using different luminescence signals of natural minerals. Quartz and feldspar minerals are mainly used, and this discussion will concentrate on these minerals.

Lower Dating Limit

Two aspects are important in discussing the lower age limit for luminescence dating:

1. Resetting of the luminescence signal prior to deposition and burial. Incomplete resetting will result in an overestimation of the burial age. Hence, it is advisable to use a luminescence signal that is rapidly reset upon light exposure. This is especially important for young samples, as the remnant age is more likely to be large compared to the burial age of the sample. As the fast-component OSL signal of quartz is most rapidly reset, quartz should be the mineral of choice and appropriate methods should be used to maximize the contribution of the fast component to the net

- signal used for analysis (Cunningham and Wallinga 2010). Madsen and Murray (2009) review the dating of young sediments and show successful application to deposits less than 10 years old.
2. Luminescence sensitivity. The luminescence sensitivity of the quartz or feldspar minerals determines the minimum detection limit of the signal. Usually this is not an important constraint, as results can be improved by measuring more aliquots and averaging results. Ages of around 10 years can be obtained, although the uncertainty tends to be large (c.50 %). In practice, the lower age limit for precise ages is a few decades (see Madsen and Murray 2009).

Upper Dating Limit

The upper age limit of luminescence dating is determined by the saturation of the luminescence signal used. Luminescence dose–response curves can usually be satisfactorily approximated by a saturating exponential Eq. (1):

$$I(D) = I_S \left(1 - \exp^{-\frac{D}{D_0}} \right) \quad (1)$$

where I is the luminescence signal intensity (after background subtraction), I_S is the saturation level, D is the absorbed radiation dose, and D_0 is indicative of the onset of saturation, i.e., it characterizes the shape of the curve. For high doses, the luminescence signal approximates the saturation level and hardly increases with dose and cannot be used to reliably infer the burial dose. Wintle and Murray (2006) suggested that reliable burial dose estimation is limited to the area below $2 \cdot D_0$, and this (arbitrary) criterion is generally applied. In some cases, dose–response curves show an additional saturating exponential component or linear component with continued growth at very high doses. However, the suitability of these components for dating has not been established (Murray et al. 2008), and using this region for dating is therefore not advisable.

Saturation doses for the fast component of the quartz OSL signal vary between samples, with average $2 \cdot D_0$ values around 150 Gy. The resulting age range depends on the dose rate for the sample, but is usually no more than 150,000 years. However, due to sample-to-sample differences in both saturation levels and environmental dose rates, the upper age limit for quartz OSL dating can widely vary and may extend up to 400,000 years (Wallinga et al. 2007).

Extending the luminescence age range is possible by using other luminescence signals, either from quartz or from feldspar. A range of methods have been proposed that use luminescence signals from quartz that saturate at higher doses. Although promising results have been obtained using thermally transferred OSL (reviewed by Duller and Wintle 2012), and violet stimulated luminescence (VSL, Ankjaergaard et al. 2013), these methods are still in development and should be further tested before routine application is feasible.

Feldspar IRSL signals saturate at higher doses than the fast-component OSL signal of quartz, but the application of feldspar dating has long been held back by athermal instability of feldspar luminescence signals (“anomalous fading,” e.g., Wallinga et al. 2007). Recently, these problems have been largely overcome using elevated temperature post-infrared IRSL signal (Thomsen et al. 2008). Post-IR IRSL methods have recently been tested and applied and are now routinely determining ages up to approximately 500,000 years (e.g., Thiel et al. 2011; Buylaert et al. 2012; Kars et al. 2012). Excellent agreement between post-infrared IRSL dating and coupled ESR/ $^{230}\text{Th}/^{234}\text{U}$ dating of tooth enamel at Mala Balanica cave in Serbia (Rink et al. 2013) further supports the use of this method near 500,000 years. Following these encouraging findings, we expect post-infrared IRSL dating methods to be further developed in the near future and be widely

used for dating Quaternary sediments. However, the method is less suitable for younger deposits as the post-infrared IRSL signal is not readily bleachable (Kars et al. 2014), which could potentially result in age overestimation.

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Tsunamigenic Sediments

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Synonyms

[Tsunami deposits](#); [Tsunami sediments](#); [Tsunamiite\(s\)](#)

Definition

Sediments eroded, reworked, transported, and deposited by a tsunami often generate deposits referred to as of tsunamigenic origin, hence tsunamigenic sediments. They are a result of tsunami inundation pending coastal conditions and availability of material. Tsunami deposits contain “exotic” materials of allochthonous provenance when compared to the sediments present at the location the tsunami struck.

Tsunami deposits are considered primary paleoseismic evidence when generated coseismically and can also be defined as off-fault instantaneous stratigraphic expressions of tectonic deformation (McCalpin 2009).

Tsunami is a Japanese word meaning “harbor wave” and was adopted by the scientific community to define long-period waves generated by the sudden vertical displacement of a large volume of water within a water basin (e.g., estuary, lake, sea, ocean).

Geological Signatures

In order to understand the significance of and date any catastrophically produced event, it is important to understand the sedimentological product (Einsele et al. 1996). Despite their potential destructive and erosive power (i.e., creation of geomorphic features), tsunamis can also generate stratigraphic expressions as a result of deposition of tsunamigenic sediments. The magnitude of the tsunami may be determined by the significance of the evidence (i.e., extent, thickness, and geometry of the deposit, type of sediment) and the degree of destruction on land, a reflection of the transport and deposition mechanism. The principal objective of the study of the sediments generated by a tsunami is to identify previous and ancient (paleo) tsunami events. Tsunami interpretation is dependent on the quality of both ancient and modern analogs. Hence, the geological signatures produced by tsunamis provide key evidence that neither the written, instrumental records, nor models alone can supply.

The worldwide abundance of tsunami deposits is considered moderate despite the magnitude of the events themselves. The study and interpretation of the sedimentological record left by a given tsunami is one of the less developed but yet most interesting subfields of paleoseismology, or the

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study of ancient earthquakes (Shiki 1996; Michetti and Hancock 1997; Shiki et al. 2000). Evidence of tsunami deposits can be found in many forms and diverse locations, both onshore, in subaerial and subaqueous environments, and offshore (submarine environment), provided availability of material to entrain and generate the deposit itself and a successful preservation. The latter applies when the burial process is rapid, and disturbance by external factors (e.g., bio- and geo-turbation, reworking, erosion, tectonic uplift) is minimal or nonexistent.

Tsunamigenic sediments can present a diversity of litho- and biofacies combinations, not always existent contemporaneously. There are a multitude of characteristics inherent to tsunami deposits, from variations in the distribution of facies to particle size range and composition. These characteristics are identifiable using several geological, biological, and chemical methodologies, amid others; however, not a single proxy can be used *solo* without any doubt (Atwater et al. 1995; Chagué-Goff et al. 2011; Goff et al. 2012).

Turbulent onrushing waters may carry mud, sand, gravel, marine organisms, and organic debris far inland, but also the ebb can transport material far offshore. Both tsunami run-up and backwash are responsible for creating different sedimentary facies that may not be present contemporaneously throughout the deposit, hence the impossibility of assigning a single prototype to tsunamigenic sediments and the difficulty in their identification and even recognition (Shiki et al. 2008). They are generally deposited as flow slackens and ebbs, in subaerial environments, and as waters calm and material falls by gravity, in the subaqueous realm. Based on geological evidence recovered from paleo-tsunamis, in addition to observations of modern tsunami deposits, the general characteristics can be described as follows (e.g., Atwater et al. 1995; Dominey-Howes et al. 2006; Chagué-Goff et al. 2011; Goff et al. 2012; López 2012; Ramírez-Herrera et al. 2012):

1. They thin and fine landward and upward in the sequence.
2. They rise landward and away from shore.
3. They may show graded bedding, reflecting both tsunami landward flow and backwash flow.
4. They may show poor sorting if compared to storm deposits.
5. They may show cross-bedding, reflecting landward and seaward currents.
6. The complex backwash deposit may show imbrication of large clasts or shells, evidence of a seaward direction of the flow.
7. The grain size distribution may be bi- or multimodal.
8. Association of multiple coarse/fine couplets is indicative of deposition by successive waves of a tsunami wave train (i.e., periodicity).
9. Microfossil assemblages of foraminifera and diatoms are incorporated, confirming the marine (pelagic and/or benthic species) provenance of the material.
10. Heavy and magnetic minerals are common.
11. The geochemical signature may show higher concentrations of certain elements not common in the embedding sediments.
12. Driftwood and plant detritus are associated with the deposit.
13. Sharp undulating basal contacts, basal load structures, and rip-up or intra-clasts of reworked underlying material (e.g., peat) are indicative of flows with great energy (i.e., turbulent), capable of erosion.
14. The thickness and lithofacies may vary accordingly to the original land surface undulation.
15. Deposits in estuarine and tidal marsh environments are well sorted compared to the chaotic character of the lacustrine ones.

16. A broad range of ages obtained from a single tsunami deposit may suggest a “cannibalistic” behavior during inundation (i.e., reworking, truncation, erosion, and mixing of previously deposited sediments).
17. Stratigraphic position may or may not indicate coseismic subsidence in tectonically emerging coasts, hence origin of the tsunami.

Onshore Deposits

Sedimentary records generated by tsunami inundation onshore subaerially may provide accurate quantitative data that can show precise limits of tsunami inundation and geographical extent for the subsequent generation of tsunami inundation models, provided that correct identification and characterization have been made. Their size and thickness depend upon the size of the tsunami event, its run-up, and the bathymetry/morphology of the locale. Estuaries, fjords, enclosed bays, lagoons, and freshwater lakes along the coast (i.e., subaqueous environments), as well as beaches, coastal flats, marshes, and wetlands (i.e., subaerial environments), can be favorable environments for tsunami wave overwash and related sedimentation.

Besides the characteristics previously described, tsunamigenic sediments are frequently deposited on low-lying coastal subaerial environments as continuous and discontinuous sheets of unconsolidated sediment (from silts to boulders) mixed with organic debris of both terrestrial and marine origin. Normally, these allochthonous tsunami-laid sheets sharply overlay the surface, creating erosional features along its sedimentary contact. They can be of millimeter scale to massively bedded and be poor to well sorted, depending on the sediment availability at the locale. They can be found intercalated by any type of sediment of local origin (e.g., peat, soils, eolian sands, and fluvial or coastal sediments). Intercalation of a series of tsunami and paleo-tsunami deposits and in situ units within the same locale (similar to a layered cake) is a sign of multiple occurrences of modern and ancient tsunami events in the area.

Coastal subaqueous environments may offer an excellent setting for deposition and preservation of tsunami-entrained materials due to the confined nature of the water body, the lacustrine realm being the most favorable one. Distinct sand or coarser material layers can be easily identified intercalated amid low-energy muddy or gyttja layers typical of lakes. The degree of particle size variation determines the hydrodynamic conditions during the event, as well as the multiple-wave incursions into the calm lacustrine basin. Coupling of layers, repetitions, and intercalations are common to tsunami deposits in lakes (e.g., Bondevik et al. 2005; López 2012). Fining-upward sequences of allochthonous materials are a result of particle settling within the water column, during the waning stages of the tsunami. An organic-rich layer may be capping the tsunamigenic sequence due to the different density-settling velocities of siliciclastic particles versus the lighter organic debris (López 2012). Depending on the size of the (semi-) enclosed coastal water body, characteristics typical of submarine tsunami deposits may also be present.

Offshore Deposits

Submarine tsunami deposits are lesser known due to the difficulties related to investigate such realm. Nonetheless, preserved submarine evidence has been found in open bays, continental shelves, and forearc basins, at water depths ranging from 10–20 to about 200 m (e.g., Fujiwara et al. 2000; Bondevik et al. 2005; Shiki et al. 2008). Recent discoveries have also pointed to shallow (3–40 m depths) continental shelves as novel areas with the potential to preserve tsunamigenic sediments (e.g., Van der Bergh et al. 2003; Abrantes et al. 2005; Reinhardt et al. 2006; Smedile et al. 2011). This nearly untapped source for tsunamigenic evidence has proved to be rich and diverse but also intricate due to the hydrodynamics present in the upper continental shelf.

Offshore submarine tsunamigenic sediments may show intercalations of coarser allochthonous sedimentary particles, intermixed with shells and terrestrial plant fragments, embedded within mud layers typical of deep-sea environments (Fujiwara et al. 2000). As a characteristic of the erosive traction force of the tsunami, the bottom contact of the event layer is usually a sharp erosional contact. Textural and structural characteristics may also reveal the underwater conditions of deposition. Cross-stratification, imbrication of larger particles (pebbles and/or shells), and wedge-shaped laminations are typical. Similar to the coastal subaqueous environments, deposition of tsunamigenic materials is characterized by settling from suspension in the water column, hence the fining-upward resulting sequence. Multiple fining-upward sequences or alternating layers of coarser siliciclastic-rich layers and organic-rich caps are evidence of multiple tsunami run-ups and backwash episodes (Fujiwara et al. 2000; Tada et al. 2002; Lawton et al. 2005; Fine et al. 2005).

Dating Tsunamigenic Sediments

The contribution of tsunamis in the sedimentological record depends on the periodicity of the event. The assessment of tsunami risk is strongly dependent on the recurrence cycle of the triggering mechanisms (e.g., earthquake, volcanic eruption, landslide). Constructing a robust chronology of tsunami events and linking them to their potential triggers is one of the most challenging issues in paleo-tsunami research but of vital importance in the quantification of the potential risk to coastal communities. Documenting the tsunami history of a particular location depends on the proper identification of tsunamigenic events in the stratigraphic record. After correct characterization, there are a number of geochronological methods that can be applied to establish the moment of deposition of tsunami-laid sediments.

The periodicity of the tsunami event in a given region may be determined by obtaining an accurate age on a series or succession of preserved tsunami deposits. This is key in determining not only the recurrence interval of past tsunami events in any particular region (e.g., Atwater et al. 1995) but also in elucidating the potential timing of future events and establishment of tsunami hazard prevention plans accordingly.

Historical and modern tsunamigenic sediments can be dated by using historical or witness accounts and historical numerical data (seismic and tidal instrumental records). The latter can only be used for relatively recent events (e.g., since the 1900s). The lack of historical numerical data enhances the value of older written records and aboriginal traditions, archaeological remains, as well as paleoseismic evidence. For prehistoric paleo-tsunami sediments, ages can be obtained by various numerical absolute dating techniques such as radiocarbon, cesium-137, and optically stimulated luminescence (Atwater et al. 1995; Huntley and Clague 1996; Clague et al. 2000; López and Bobrowsky 2001; Donato et al. 2008; Reinhardt et al. 2006; López 2012).

Tsunamigenic sediments are chaotic anomalous layers enriched in a diversity of allochthonous materials of both inorganic and organic origin. Transport, erosion, reworking, and redeposition of organic debris and biological materials (shells) decrease the probabilities of obtaining accurate ages of the sediments. Organic materials (e.g., wood and plant detritus or shells) may have much older ages than that of the tsunamigenic deposit itself, making the age determination difficult. In order to reliably date a tsunami deposit using biological materials, it is important to find them in accordance with the deposition context, i.e., in situ, for example, tree trunks or intact bivalve mollusk shells killed and buried by the tsunami. Archaeological remains, whenever available, may be of more service only when identifiable pieces (e.g., pottery shards, coins) have remained in pristine conditions and in situ (the material has not been moved from its archaeological context). In addition, over

time, cultural material may be reworked, eroded, and incrustated with organisms, losing its identification potential, hence its dating value.

Due to the above, the reliability of using ^{14}C can be at stake when dealing with reworked and redeposited material such as plant detritus and shells within the tsunami deposit. Old carbon (e.g., fossils, coal, older carbon-rich bulk samples) associated with the reservoir effect can contaminate the deposit when introduced by erosion or redeposition. For example, as a global average, marine shells have a mean reservoir age of 400 years. Young carbon (e.g., live roots) can also contaminate tsunami sediments when these are older than the modern surface in which the root in question is growing.

In terms of dating relatively modern and historical tsunami deposits, numerical dating techniques such as ^{210}Pb and ^{137}Cs can be used (e.g., Miller et al. 2013), provided that an age-depth model is constructed. Such methods imply high-resolution sampling down-core or of the exposed outcrop surface with the purpose of building an activity curve showing the nuclide's peak at a particular depth (normally close to the surface) and exponential decay down-core. Both nuclides' activity down-core extrapolation curves are mostly used for sediment accumulation rate assessment but may also reveal the presence of major event layers such as tsunami deposits (rapid deposition or coarser particle size fractions imply no down-core change on the activity profile or depletion of the nuclide). Unfortunately, both dating techniques generally only work in clay- or silt-rich sediments deposited in the last 250 years. Lead-210 is a short-lived nuclide with a half-life of 22.3 years and is a product of the decay of ^{222}Rn in the uranium radioactive chain. It only remains a few days in the atmosphere before falling out on the earth's surface. Successful ^{210}Pb dating of tsunami sands has been achieved for the 1945 Makran tsunami (Arabian Sea; Miller et al. 2013) and the 2004 Indian Ocean tsunami (Thailand; Sakuna et al. 2012). Cesium-137 can only be used for very recent events as it was produced by atmospheric nuclear testing between 1952 and 1972, with peak productions in 1963–1964 (Woodward 1964; Wan et al. 1987; Naidu et al. 1999).

Optically stimulated luminescence (OSL), also known as optical dating (Huntley et al. 1985), was first used by Huntley and Clague (1996) to date tsunami-laid sands on coastal areas of Vancouver Island, Canada, and Puget Sound, Washington, USA. In OSL, due to the fact that the luminescence signal is directly related to light exposure, the exposure of mineral grains to light in a subaqueous environment can be proportionally related to the (hydro-) dynamic processes, i.e., the erosion-reworking-transport-deposition cycle. During this cycle, a mineral grain could be sufficiently exposed to daylight erasing (zeroing) any previously accumulated luminescence signals before its “final” burial. This zeroing process is the backbone of optical dating. More importantly, OSL provides accurate direct dating of the tsunami-laid sediment itself, provided that incomplete zeroing does not mask the luminescence signal of the tsunami event.

OSL dating of beach and underwater littoral sediments has been proven successful in various regions of the world as they can be as effective zeroing environments as the eolian. Several tsunamigenic sediments have been dated with OSL with various degrees of success, for example, the 1755 Lisbon tsunami (Banerjee et al. 2001), historical and paleo-tsunamis on the west coast of the USA (Huntley and Clague 1996; Ollerhead et al. 2001), the ancient 115 A.D. Mediterranean tsunami found in a submerged archaeological site in Israel (Reinhardt et al. 2006), Australia (Switzer and Jones 2008), the Andaman Islands (Kunz et al. 2010), and the 2004 Indian Ocean tsunami sediments in Thailand (Prendergast et al. 2012).

Nonetheless, as recently discovered by Ramírez-Herrera et al. (2012), tsunamigenic sediments can be deposited during nocturnal conditions, obstructing all chances of luminescence signal zeroing. Moreover, due to their distinctive hydrodynamically chaotic behavior, often complicated shallow marine and coastal pathways (Einsele et al. 1996), the level of turbidity of their waters, and their relative short transport time, tsunamis may not allow for sufficient zeroing of the sediments

they entrain, move, and deposit. Hence, dating tsunamigenic sediments by means of OSL can be a challenge, however, possible even in difficult conditions such as in underwater archaeological settings where anthropogenic reworking is most probable (e.g., Reinhardt et al. 2006). In such conditions of chaos and heterogeneity of material, it is always recommended to use multiple dating methods in conjunction with OSL to better constrain the age of the targeted tsunamigenic sediment.

In the event that a tsunamigenic sediment itself cannot be dated using absolute geochronological methods such as ^{14}C , ^{137}Cs , ^{210}Pb , OSL, or historical records, relative dating should be used. This is needed when difficulties arise in finding appropriate datable materials within the tsunami deposit, or even due to their “cannibalistic” character (i.e., intense mixture of multi-provenance materials, hence broad age range). Bracketing the age of a tsunami deposit by dating the immediately underlying and overlying sediment is a viable solution. Chronological techniques such as tephrochronology, biostratigraphy, and dendrochronology have provided excellent bracketing ages for paleo-tsunami deposits (e.g., Atwater et al. 2005; De Martini et al. 2010), as well as correlation with neighboring archaeological artifact materials, so at least a *terminus ante quem* age can be determined.

Summary

The identification and characterization of tsunamigenic sediments are the principal objectives in the corroboration of any tsunami event occurrence. Nonetheless, due to the diverse nature of the deposits, i.e., overwash versus backwash and onshore versus offshore, tsunami sediments are not easily recognizable, let alone identifiable, based on a unique criteria. Multi-proxy approaches pertaining to various fields of research (e.g., geology, biology, archaeology, hydraulics, geochemistry) are to be used combined to better detect these ephemeral, chaotic, yet catastrophic tsunami products.

Tsunamigenic sediments are key to establish geographical correlations of tsunami events and their triggering mechanisms. Without an accurate correlation of events, no real determination of inundation limits, magnitude of the event, danger-prone areas, and extent of the risk can be assessed. Quantification of ancient tsunami events relies on the existence of the geological evidence. Calculation of how often these events occur, hence recurrence intervals, depends on the precise dating of the latter. Without a correct chronological analysis of both historical and paleo-tsunami deposits, the implementation of adequate risk assessment and disaster prevention plans may be at stake.

Cross-References

- ▶ [\$^{14}\text{C}\$ Dating](#)
- ▶ [\$^{210}\text{Pb}\$ Dating](#)
- ▶ [Dendrochronology, Surficial Processes](#)
- ▶ [Luminescence, Coastal Sediments](#)
- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating, Single Grain Dose Distribution](#)
- ▶ [Quartz](#)
- ▶ [Relative Dating Methods](#)
- ▶ [Tephrochronology](#)
- ▶ [Walther's Law of Facies](#)

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Uranium-Lead, Chemical Isochron U-Pb Method (CHIME)

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Synonyms

Chemical dating; CHIME dating; CHIME method; EMP dating; EPMA dating

Definition

The chemical (Th-U-Pb) isochron method (CHIME) involves dating of micrometer-scale monazite, xenotime, zircon, and other minerals by electron probe microanalyzer (EPMA). Ages are obtained through analysis of multiple spots within and between mineral grains in polished thin sections or grain mounts. If the domains analyzed are consistent in age within the precision of measurement and have sufficient variation in Th and/or U content, then the data can be used to construct an “isochron” from which an age can be obtained via linear regression. This method, especially when coupled with data screening by chemical criteria, can produce accurate and moderately precise ages of mineral growth. It has the advantages of being nondestructive, of high spatial resolution, achievable with widely available electron microprobe instruments, and workable on minerals with non-radiogenic (or initial) Pb contents. In addition to spot analysis, electron microprobe dating can be conducted over areas defined by stage stepping, providing maps that discriminate chemically and chronologically distinct domains within monazite as young as 100 Ma.

Introduction

Current age dating methods based on mass spectroscopy (TIMS, SIMS, LA-ICPMS) rely on isotopic analysis to calculate age estimates. The robustness of age estimates can be tested against the criterion of “concordance,” or equivalence of age estimates from independent parent-daughter isotope pairs (e.g., between ^{238}U - ^{206}Pb , ^{235}U - ^{207}Pb , and ^{232}Th - ^{208}Pb). Prior to the widespread availability of such instrumentation, the concept of a “chemical age,” where proportions of total (non-isotopic) U, Th, and Pb were used to calculate age estimates, was applied to the dating of U- and Th-rich rocks and minerals. The chemical age requires assumptions that all Pb present in the sample is radiogenic, a product of the in situ decay of Th and U, and that no Pb has been added or lost from the sample since formation. Such assumptions are problematic, since many minerals include non-radiogenic Pb; in addition, Pb can be mobilized through several geological processes, including heating during metamorphism, hydrothermal activity, and weathering. Some Th- and/or U-bearing minerals, however, incorporate little to no Pb when grown and are relatively robust with respect to Pb isotope systematics under most crustal conditions. The orthophosphate minerals monazite and xenotime, which can incorporate U and Th on the order of several weight percent, typically retain

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concordant isotope systematics. Zircon is less robust, with an ability to retain radiogenic Pb that strongly depends on the degree of radiation damage accumulated by the mineral; nonetheless, relatively young or low-U zircon does typically retain concordant isotope systematics, either in whole crystals or in micrometer-scale domains within grains that are analyzable by microbeam techniques. These and other U- and Th-bearing minerals are common in most crustal rocks, but typically in accessory amounts only and as grains tens to hundreds of micrometers across. Consequently, they are most suited to microbeam analysis, including chemical dating by EPMA in conjunction with an effective correction for initial Pb. The use of the EPMA for the chemical dating of monazite and zircon was established with the development of CHIME (Suzuki et al. 1991; Suzuki and Adachi 1991a, b), as outlined below. Analytical refinements and variants on the statistical handling of EMPA data to produce age estimates have been developed since (see below, as well as Suzuki and Kato 2008, and references therein). The technique need not be restricted to the electron microprobe; Kusiak and Lekki (2008) utilized a proton microprobe for CHIME dating of monazite, which provides potentially greater peak-to-background sensitivity than EPMA. Age-mapping techniques also have been introduced to reveal the geometry and distribution of growth stages within monazite grains (Williams et al. 1999).

Age Calculation

The amount of Pb that has accumulated in a U-Th-bearing mineral, relative to the amount of U and Th remaining, is given by

$$\begin{aligned} &^{232}\text{Th}, ^{235}\text{U} \text{ and } ^{238}\text{U} : \\ \text{Total Pb} &= \text{Pb}_i + ^{208}\text{Pb} + ^{207}\text{Pb} + ^{206}\text{Pb} \\ &= \text{Pb}_i + ^{232}\text{Th} \{ \exp(\lambda_{232}t) - 1 \} + ^{235}\text{U} \{ \exp(\lambda_{235}t) - 1 \} + ^{238}\text{U} \{ \exp(\lambda_{238}t) - 1 \} \end{aligned} \quad (1)$$

where Pb_i is the initial (non-radiogenic) Pb, t denotes the time after crystallization, and λ_Z are the decay constants $\lambda_{232} = 4.9475 \times 10^{-11} \text{ year}^{-1}$, $\lambda_{235} = 9.8485 \times 10^{-10} \text{ year}^{-1}$, and $\lambda_{238} = 1.55125 \times 10^{-10} \text{ year}^{-1}$ (Steiger and Jäger 1977). Equation (1) is simplified using $^{238}\text{U}/^{235}\text{U} = 137.88$ (Steiger and Jäger 1977) in

$$\begin{aligned} \text{Total Pb} &= \text{Pb}_i + \text{Th} \{ \exp(\lambda_{232}t) - 1 \} \\ &+ \text{U} [\{ \exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t) \} / 138.88 - 1] \end{aligned} \quad (2)$$

If Pb_i is assumed to be zero, we can calculate an age from a single set of Th, U, and Pb measurements. This assumption, however, is not self-evident. In the CHIME procedure, we first calculate an apparent age from each set of ThO_2 , UO_2 , and PbO determinations (as wt%) by solving the age equation:

$$\begin{aligned} \text{PbO}/W_{\text{Pb}} &= (\text{ThO}_2/W_{\text{Th}}) \times \{ \exp(\lambda_{232}t) - 1 \} \\ &+ (\text{UO}_2/W_{\text{U}}) \times [\{ \exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t) \} / 138.88 - 1] \end{aligned} \quad (3)$$

where W symbolizes the gram-molecular weight of each oxide: $W_{\text{Th}} = 264$ ($232 + 32$), $W_{\text{U}} = 270$ ($238 + 32$), $W_{\text{Pb}} = 224$ ($208 + 16$) for Th-dominant minerals and $W_{\text{Pb}} = 222$ ($206 + 16$) for U-dominant minerals. Taking the apparent age, we convert the sum of measured ThO_2 and UO_2 into ThO_2^* (for Th-dominant minerals) or UO_2^* (U-dominant minerals) as follows:

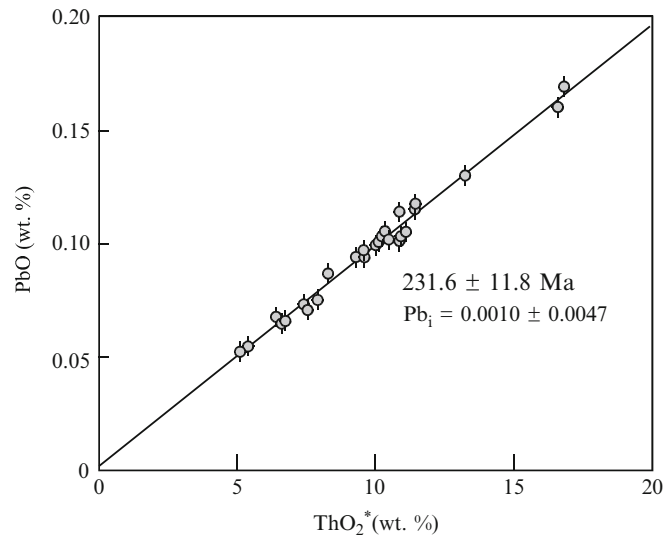


Fig. 1 Plot of PbO versus ThO₂* for monazite grains in a granite sample from the Hida metamorphic belt, central Japan (Suzuki and Adachi 1991b). Error bars in the figure represent 1σ analytical uncertainty, and errors referred for the age and Pb_i (intercept) are 2σ

$$\text{ThO}_2^* = \text{ThO}_2 + \text{UO}_2(W_{\text{Th}}/W_{\text{U}}) \times [\{\exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t)\} / 138.88 - 1] / \{\exp(\lambda_{232}t) - 1\} \quad (4a)$$

$$\text{UO}_2^* = \text{UO}_2 + \text{ThO}_2(W_{\text{U}}/W_{\text{Th}}) \times \{\exp(\lambda_{232}t) - 1\} / [\{\exp(\lambda_{235}t) + 137.88 \exp(\lambda_{238}t)\} / 138.88 - 1] \quad (4b)$$

Minerals such as monazite or zircon that grew during a single geological event can vary significantly in Th and U content, both between and within grains. If these have consistent amounts of Pb_i and have remained closed to Pb loss or gain, all analytical data will form a linear array (Fig. 1), with the slope (m) and intercept (b):

$$\text{PbO} = m \times \text{ThO}_2^* + b \text{ (Th-mineral)} \quad (5a)$$

$$\text{PbO} = m \times \text{UO}_2^* + b \text{ (U-mineral)} \quad (5b)$$

We determine the best-fitting regression line through the procedure proposed by York (1966), taking account of uncertainties in the microprobe analyses, and calculate the first estimation of age (T) from the slope (m) of equations:

$$T = \ln \{m (W_{\text{Th}}/W_{\text{Pb}}) + 1\} / \lambda_{232} \text{ (Th-mineral)} \quad (6a)$$

$$m (W_{\text{U}}/W_{\text{Pb}}) = \{\exp(\lambda_{235}T) + 137.88 \exp(\lambda_{238}T)\} / 138.88 - 1 \text{ (U-mineral)} \quad (6b)$$

Then, we can obtain an improved estimate by replacing the apparent ages (t) in Eq. (4) with the first age estimate (T) and iterate to the desired tolerance. The y-intercept of the line represents an average Pb_i for all data points. A significant amount of Pb_i, if present, would deviate the line from the origin; inconsistent Pb_i, Pb disturbance, or the presence of multiple age domains would result in scattering of data away from a linear array.

Variations in the mathematical treatment have been proposed by several authors. Montel et al. (1996) proposed the calculation of an age from Eq. (2) by assuming no Pb_i and estimation of a probable age from several determinations after propagating uncertainties with representation by a bell-shaped probability curve. Rhede et al. (1996) represented the age equation (2) for monazite by an equation of a plane in three-dimensional ThO_2 - UO_2 - PbO space:

$$PbO = aThO_2 + b + cUO_2 \quad (7)$$

where $a = (1/W_{Th}) \times [\exp(\lambda_{232}t) - 1]$, $b = \text{average } Pb_i$ and $c = (1/W_U) \times [\{\exp(\lambda_{235}t) + 138 \exp(\lambda_{238}t)\}/139 - 1]$. Cocherie and Albarede (2000) ignored parameter b and proposed a new $Th/Pb = f(U/Pb)$ graphical representation.

EPMA Analysis of Th, U, and Pb in Minerals

Target minerals for chemical dating include monazite, zircon, xenotime, polycrase, thorite, huttonite, uraninite, and allanite. Analysis does not differ fundamentally from the conventional method on a wavelength-dispersive-type EPMA. However, certain difficulties that are normally unimportant in major element analyses become acute in the accurate determination of Th, U, and Pb concentrations. Critical factors that affect determinations include X-ray peak interferences, background estimations, type of detector gas, collimator slit, accelerating voltages, probe currents, and count rates (Suzuki and Adachi 1991a,b; Jercinovic and Williams 2005; Suzuki and Kato 2008). Adopting 400 s integration times for a 150 nA probe current, the detection limit of PbO at a 95% confidence level is around 100 ppm. Monazite with 10 wt% ThO_2 generates around 420 ppm PbO, and zircon with 2 wt% UO_2 generates around 260 ppm PbO in 100 Ma. Thus EPMA dating can provide monazite and zircon ages younger than the Cretaceous period. Imayama and Suzuki (2011) successfully dated Miocene monazite by adopting a 3,200 s integration of counting at peak and background positions.

Chemical Criteria for Screening of EPMA Data

Monazite $((Ce, La, Nd, Y) PO_4)$ commonly contains significant brabantite $((Th, U)Ca(PO_4)_2)$, huttonite $((Th, U)SiO_4)$, and $CaSO_4$ substitutions. Excluding minor substitution by halogens and Sr, atomic $(Ca + Si)/(Th + U + Pb + S) = 1$, and significant deviations from this value are normally encountered only in analysis of altered or metamict portions. The $(Ca + Si)/(Th + U + Pb + S)$ value therefore provides a criterion for probable discordance in Th-U-Pb isotope systematics (Suzuki and Kato 2008). The value may also deviate from unity if X-ray excitation overlaps with mineral grains adjacent to the target mineral; nonstructural elements, such as potassium, may also be detected. Screening of monazite analyses with these chemical criteria commonly reduces scatter in an analytical dataset. In the case of zircon, secondary alteration of radiation-damaged domains, which causes loss of radiogenic Pb and contamination by non-radiogenic Pb, is often associated with enrichment in Ca (Geisler and Schleicher 2000), so that high Ca (>0.05 wt%) zircon typically yields unreliable ages (Suzuki and Kato 2008). Thus Ca content, along with S and K, can be used as chemical criteria for the screening of zircon analyses.

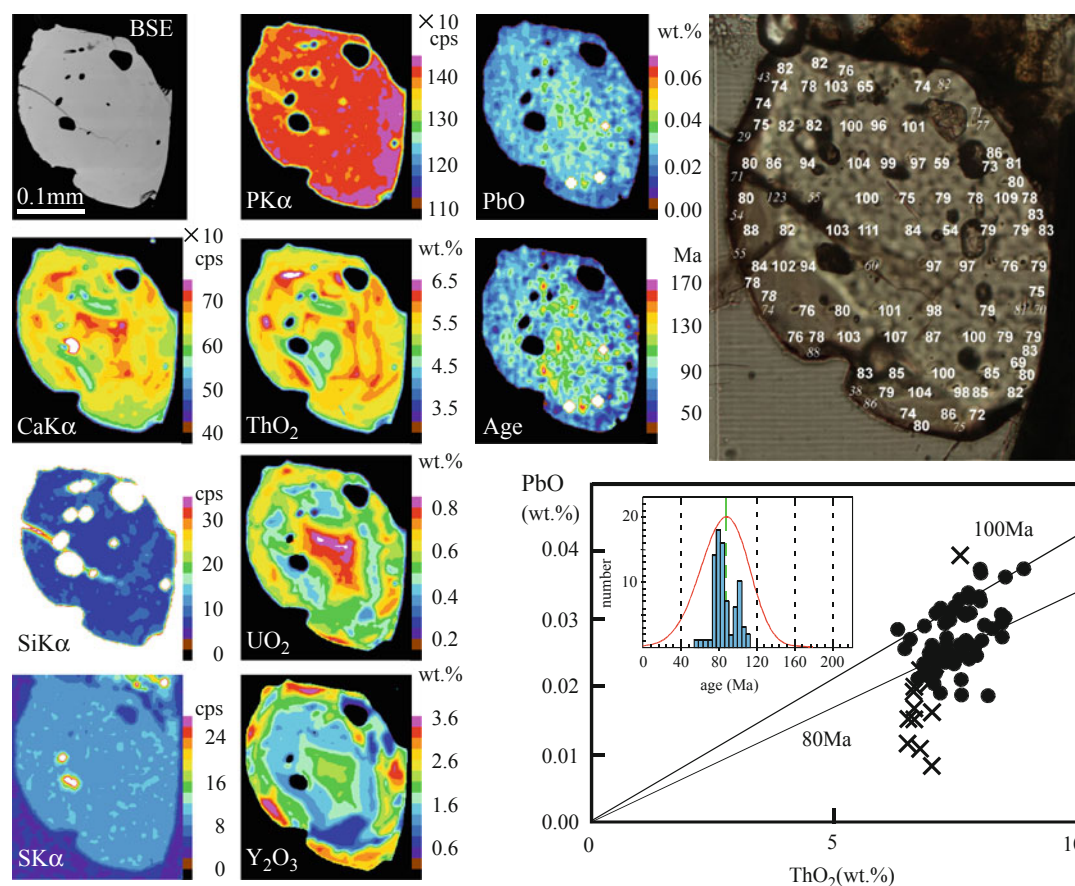


Fig. 2 Compositional and age maps of a monazite grain in migmatite from the high-temperature/low-pressure Ryoke metamorphic belt, central Japan (Kawakami and Suzuki 2011). Attached photomicrograph shows apparent ages calculated from spot analyses. Numbers in italics represent analyses rejected by chemical criteria of $0.95 < (\text{Ca} + \text{Si})/(\text{Th} + \text{U} + \text{Pb} + \text{S}) < 1.05$ and $\text{K}_2\text{O} < 0.05$ wt%

Age Mapping

The age-mapping technique highlights the geometry and distribution of age domains on the micrometer scale within individual grains (Williams et al. 1999). Depending on the intrinsic response of the EPMA detector, a dwell time of 0.5–1 s may be sufficient for monazites with 1.0 wt% PbO under 15 keV and 150 nA beam conditions. However, the dwell time required for young monazites with 300–600 ppm PbO ranges from 50 to 100 s. To shorten the mapping time, multiple spectrometers for Pb measurement can be adopted (Suzuki and Kato 2008).

The raw intensity data are corrected for background and interferences and converted into concentrations in the same way as spot-by-spot analysis (Suzuki and Kato 2008) or by calibration against standard intensities (Williams et al. 1999). The background for each pixel is obtained from the relationships between ThMα + UMβ line counts and counts at fixed offsets from spectral lines, which are determined before the measurement of Th, U, Pb, and Y intensities. Then the age of each pixel is calculated from the concentration through Eq. (2) by assuming $\text{Pb}_i = 0$, and the resulting age value is stored in the corresponding pixel of a new map. Figure 2 exemplifies age and composition maps of a young monazite grain that shows an 83.5 ± 2.4 Ma high-Y rim on a 96 Ma core (Kawakami and Suzuki 2011).

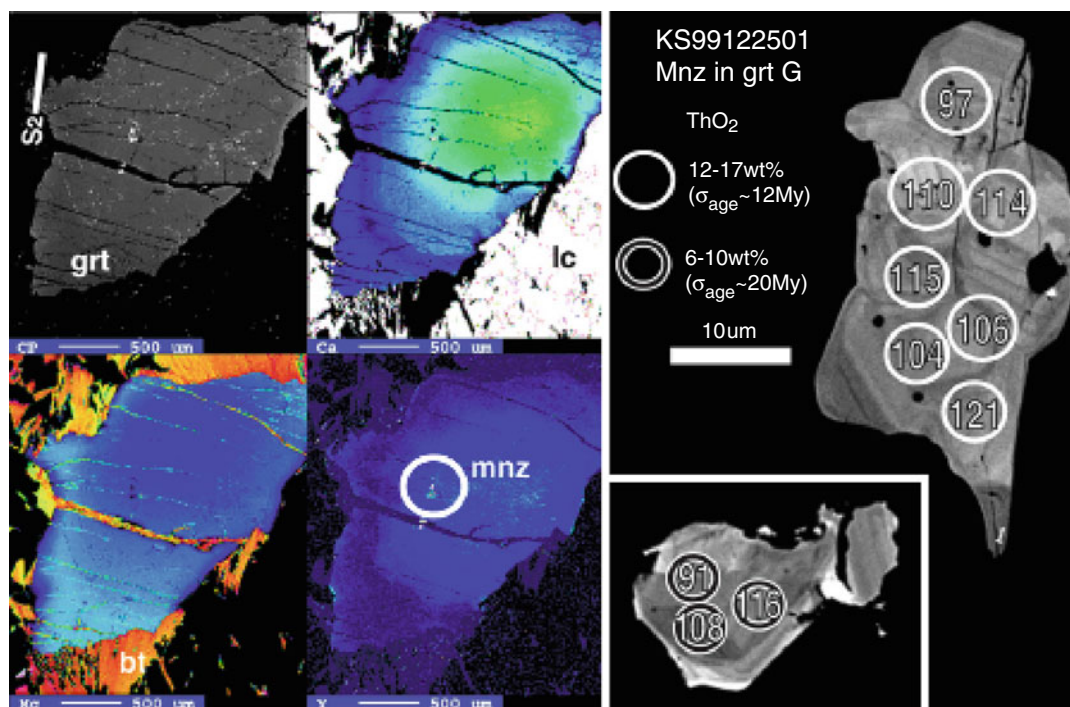


Fig. 3 BSE and WDS elemental images of garnet (grt G) and inclusions of monazite in a garnet-cordierite migmatite from the Higo metamorphic terrane of western Kyushu, Japan (From Dunkley et al. 2008)

Applications

The dating of accessory minerals by EPMA readily provides age estimates for geological events. There is, however, widespread recognition of the difficulty of assigning age data to specific events, especially in terranes which have experienced multiple episodes of high-temperature metamorphism. Grains of accessory minerals such as monazite and zircon commonly preserve reliable age data from multiple stages of growth, which need to be understood in the context of paragenetic mineral assemblages. The clearest interpretation of an age estimate requires the fewest assumptions and the support of petrographic evidence for textural and compositional equilibration. Thus, the technique is best done on datable minerals in situ, in polished thin sections where mineral assemblages are preserved.

An example of petrographically constrained CHIME dating is provided by Dunkley et al. (2008), on the Higo metamorphic terrane of western Kyushu, Japan, which underwent high-grade metamorphism during a tectonic event considered by previous investigations to have occurred in either the Permo-Triassic or mid-Cretaceous period. In this study, monazite grains were dated that occur in textural equilibrium with the peak metamorphic assemblage spinel + sillimanite + garnet + plagioclase + biotite, and aligned with a mineral foliation and gneissosity developed during peak metamorphism. Monazite grains were also found as inclusions within garnet porphyroblasts (Fig. 3), where they would be shielded from hydrothermal fluids that potentially could have disturbed Pb in monazite. The dating of monazite both in inclusions and the foliated matrix thus constrains the timing of metamorphic mineral growth. In both cases, CHIME ages of around 115 Ma were obtained.

Partitioning of Y between coexisting monazite, xenotime, and garnet allows correlation of monazite growth with garnet growth and/or consumption (Pyle et al. 2001). Figure 4 shows Y and

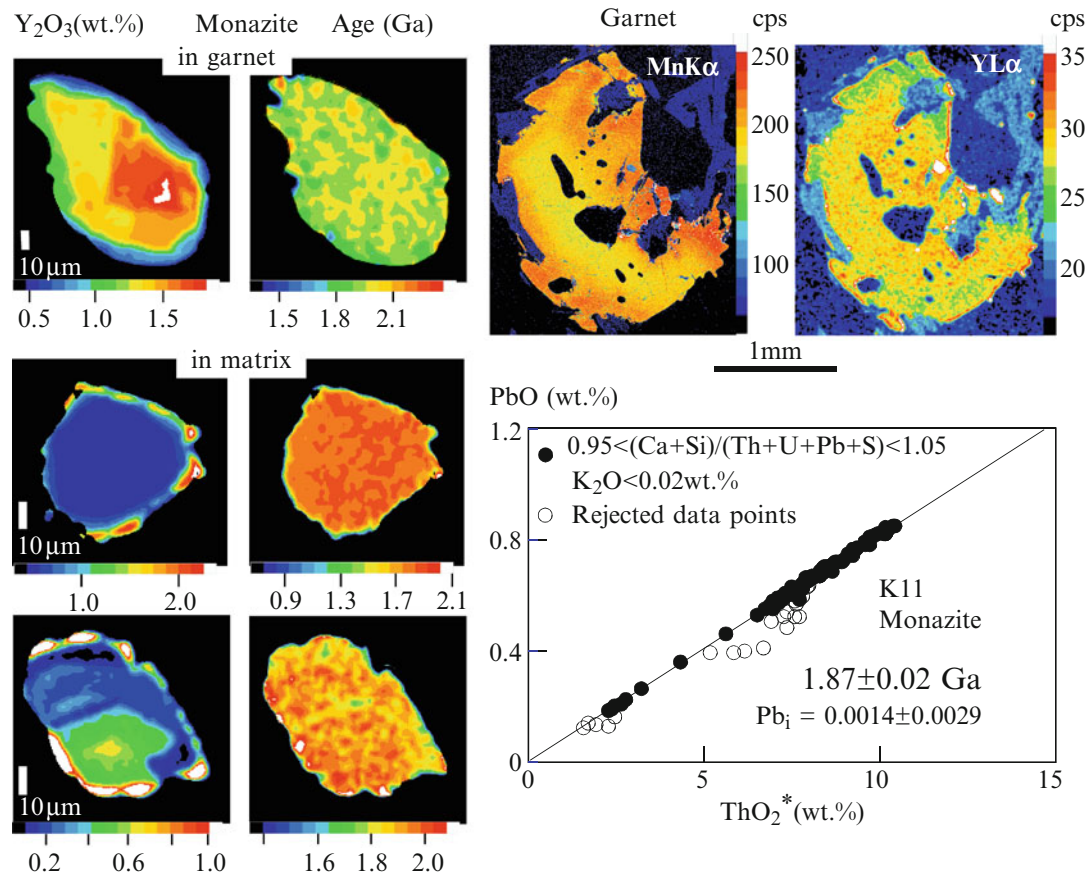


Fig. 4 Yttrium and age maps of monazite grains and MnKα and YLα maps of porphyroblastic garnet in a quartzofeldspathic granulite from the Gyeonggi massif, Korea (Suzuki 2009)

age maps of monazite and Mn and Y maps of garnet in a quartzofeldspathic granulite from the Gyeonggi massif in the Korean Peninsula (Suzuki 2009). The sample shows little evidence of a retrograde overprint beyond minor growth of biotite along garnet grain boundaries. The garnet grain decreases in Y from core to rim with peripheral Y enrichment and shows a core-to-rim increase in Mn, which can be attributed to a retrogressive modification along with biotite formation. Zoning patterns of Y differ among the monazite grains. The monazite grain enclosed in garnet shows a core-to-rim decrease in Y, and those in the matrix show a peripheral enrichment of Y on low-Y interiors. Due to the compatibility of Y in garnet, an increase in garnet growth during prograde and peak metamorphism decreases the availability of Y in the effective bulk rock. The marginal Y decrease in monazite within garnet is synchronous with an increase in garnet growth during prograde granulite-facies metamorphism. The Y-poor domains in matrix monazite have grown along with garnet, and Y-rich margins on matrix monazite grains are attributed to retrograde replacement of garnet by biotite. Age maps show no age variation between three chemical domains on individual grains, which together yield a CHIME age of $1868 \pm 24 \text{ Ma}$. The age map combined with compositional maps is a powerful tool to reveal stages of a metamorphic history within a single event.

Cross-References

- ▶ [Geochronology](#)
- ▶ [Secondary Ion mass spectrometer \(SIMS\)](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)
- ▶ [Uranium-Lead, Hydrothermal Events](#)
- ▶ [Uranium-Lead, Igneous Rocks](#)
- ▶ [Uranium-Lead, Metamorphic Rocks](#)
- ▶ [Uranium-Lead, Zircon](#)

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Uranium–Lead, Igneous Rocks

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Definition

The measurement of magma crystallization ages for volcanic and plutonic rocks using the uranium–lead radioactive decay system.

Introduction

The crust is dominated by igneous rocks, which record ancient geologic processes. Precise dating is one of the most powerful tools for understanding crust formation and is the widest application of radiometric geochronology. The ages of igneous rocks are measured by dating minerals that contain radiogenic daughter elements.

The U–Pb system is considered the most robust and useful geochronometer for igneous rocks largely because of the mineral zircon (ZrSiO_4 , Fig. 1, and Cross-Reference ► [Uranium–Lead, Zircon](#)), which contains high trace levels of U and strongly rejects Pb during crystallization. Therefore, present-day Pb within it is dominantly radiogenic. Initial Pb in a newly crystallized mineral, called common Pb, can be distinguished because it has a different isotopic composition from the radiogenic Pb. Zircon is a common and easily recoverable trace mineral in siliceous igneous rocks such as granitoid plutons and felsic volcanics that are widespread in continental and arc environments. Partial melting of older rocks buried deep in the crust may not completely destroy their zircon, which is often preserved as older cores in younger rocks that crystallize from the melt. This zircon is overgrown by a phase giving the age of the melt, while the cores preserve the age of the original rock or protolith. The presence of older zircon in a younger population is called inheritance. It can be a significant problem in age interpretation but is also a source of information on the provenance of the magma.

Other minerals favorable for U–Pb geochronology include baddeleyite (ZrO_2 , Fig. 2) and monazite (CePO_4). Baddeleyite is common in mafic rocks, such as gabbro and diabase dykes, which normally do not contain zircon. Like zircon, baddeleyite contains several hundred ppm of U and essentially no common Pb. Unlike zircon, it is resistant to Pb loss and gives accurate ages on very tiny grains. Monazite is low in common Pb, normally contains high U concentrations ($>1,000$ ppm), and is relatively resistant to Pb loss. It is however much rarer than zircon, occurring mostly in highly evolved crustal rocks such as granites produced from the melting of sediments. Titanite, rutile, apatite, perovskite, and columbite-tantalite can also be suitable for U–Pb dating but contain relatively high common Pb concentrations. The first three are common trace minerals but may be susceptible to metamorphic growth and resetting. The last two are relatively rare.

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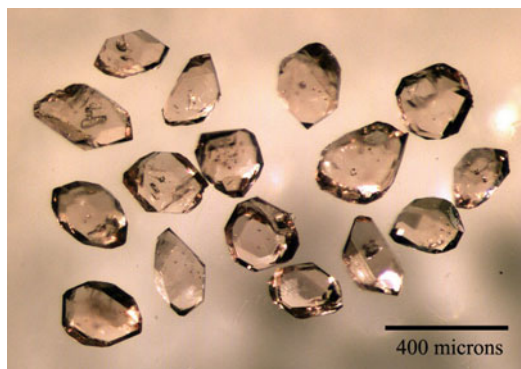


Fig. 1 Pristine zircon from a late Archean (2,732 Ma) quartz diorite in northwest Ontario, Canada

Methods

The most precise method of U–Pb dating is by isotope dilution (ID). This involves dissolving a mineral grain, chemically separating the U and Pb, and determining the amount of the isotopes by mixing them with a known quantity of an enriched isotope, called the spike, and measuring the isotopic composition. Isotopes are usually measured by thermal ionization mass spectrometry (TIMS) or multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). Methods of sample treatment were introduced for avoiding altered, disturbed zircon domains to achieve accurate results (Krogh 1982; Mattinson 2005). The secondary ion mass spectrometer (SIMS) was developed to measure ages of individual domains within polished zircon crystals at the scale of tens of microns. The earliest model is known as the SHRIMP (Compston 1999) and has continued to be developed along with other models (e.g., Rollinson and Whitehouse 2011). Laser ablation inductively coupled plasma mass spectrometers (LA-ICPMS) were developed more recently and have similar capabilities (e.g., Alves et al. 2013) although they still require more sample than SIMS and produce a deeper ablation spot (tens of microns compared to 1–2 microns for SIMS). Although spot zircon ages generally have less precision than ID analyses, they are much faster to obtain and they allow older cores and younger overgrowths to be readily dated within complex zircon grains. Currently, U–Pb ages can be routinely determined to a 95 % confidence level of about ± 0.05 % or better from single zircon grains by ID and ± 0.5 % by SIMS and LA-ICPMS from 20 to 30 micron diameter spots on polished zircon.

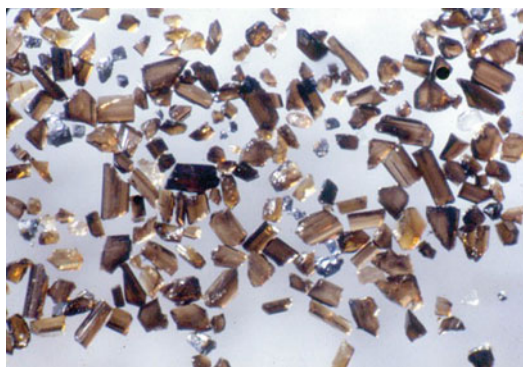


Fig. 2 Brownish baddeleyite crystals from an 1,109 Ma gabbro sill associated with the Midcontinent Rift, northwest Ontario, Canada

Applications

Precambrian Greenstone Belts

The Precambrian makes up about 80 % of geologic time but contains few fossils. It comprises the continental shields where many of the rocks are deformed into linear structures known as greenstone belts. One of the first successful applications of high-precision U–Pb dating was to unravel the chronology of Archean greenstone belts so as to understand the development of the early crust. The necessity of eliminating secondary Pb loss from zircon and achieving the age accuracy required to resolve timing of eruptions within an average greenstone belt (about ± 1 Ma) was a major incentive for developing the air abrasion method for achieving accurate results on zircon (Krogh 1982) and for improving chemical separation methods so that single grains could be dated. Much of this early work was carried out in the Superior Province (e.g., Corfu et al. 1989; Davis et al. 1989). It provided evidence for a north to south progression of late plutonism and deformation, suggesting that the craton formed by accretion of oceanic arc and micro-continental terranes through plate tectonic processes broadly similar to those operating today.

Geologic Time Scale

The geologic time scale was historically based on relative dating of sedimentary rocks using fossils that can be correlated from units in different areas and ranked in relative age using superposition of stratigraphically higher (younger) over lower (older) units. Arthur Holmes promoted the early development and application of U–Pb dating and was able to publish surprisingly accurate ages for the principal geologic periods in his booklet “Age of the Earth” (1927). At this time, before precise mass spectrometry, it was necessary to use chemical methods to measure U and Pb in rare highly radioactive minerals found in granites and pegmatites. Determining time intervals and rates of geologic processes requires the most precise ages, and a great deal of recent work is directed toward dating important fossil-based marker units, such as mass extinction boundaries. Possible correlations with large igneous and meteorite impact events can be tested using precise geochronology in order to understand the driving forces of evolution. This work requires precisely dated zircon from thin volcanic ash layers within sedimentary rocks. Early work on the Paleozoic time scale was carried out by Tucker et al. (1990) using ID-TIMS and Compston and Williams (1992) using SIMS. This led to much debate over discrepancies that were later traced to problems, now resolved, with the SIMS standard zircon.

The largest known mass extinction occurred at the end of the Permian period just before the beginning of the Triassic. Well-preserved stratigraphic sections in China contain numerous volcanic ash beds in latest Permian strata that have been a focus of recent work in precise zircon dating. They have allowed the extinction event to be dated at 252.28 ± 0.08 (Shen et al. 2011). Volcanic and plutonic rocks associated with the early stages of the Siberian flood basalts, the largest known volcanic province, have given similar ages (Kamo et al. 2003). This coincidence suggests that the extinction was caused by a rapid increase in atmospheric CO₂ level at the beginning of volcanism and therefore that major igneous events can cause mass extinctions. A similar correlation has been found between the Triassic-Jurassic extinction at 201.3 ± 0.2 Ma and eruption of the Central Atlantic magmatic province at 201.38 ± 0.02 Ma (Schoene et al. 2010). The necessity of achieving the highest possible levels of precision for dating such samples was a major driving force for developing the chemical abrasion method to isolate pristine zircon (Mattinson 2005).

Plutonism

The proportional error of U–Pb ages is approximately independent of the absolute age, so that the absolute error is smaller in younger rocks. While age errors not much better than ± 1 Ma can be routinely achieved for Archean rocks, errors of ± 0.1 to ± 0.01 Ma can be achieved for ages of 100 Ma or younger. This has allowed detailed study of the construction of young composite felsic intrusions such as in Leuthold et al. (2012), Schoene et al. (2012), and Matzel et al. (2006) where the age range for batholith emplacement was determined by dating individual plutonic phases with errors of 10–50 Ka. A similar study successfully resolved emplacement of components of the 56 Ma Skaergaard layered mafic intrusion over a time scale of 100 Ka (Wotslaw et al. 2012). Such studies reveal details that were masked by the limited precision of earlier dating. Emplacement and crystallization of large plutons can no longer be considered instantaneous but are seen to proceed over a time span of tens of thousands of years during which different generations of zircon crystallize (autocrysts from extended crystallization within a magma chamber and antecrysts from earlier batches of magma), in addition to much older zircon incorporated from host rock (xenocrysts).

Ages of Ophiolites and Ocean Crust Accretion

Basalt is the most common rock type on Earth's surface, but most of it is found in the oceanic crust, which is continually being produced at mid-ocean ridges and recycled into the mantle at subduction zones. Consequently, the oldest parts of actively spreading ocean crust are only about 200 Ma, far younger than ages preserved on unsubductable continental crust. However, fragments of ancient oceanic crust have in the past been thrust onto continents and preserved from subduction. Such fragments are called "ophiolites." Most are thought to have originated in small ocean basins that formed in extensional environments between oceanic arcs and continental margins. They were thrust (obducted) onto the adjacent continent in continental collision zones. Some ophiolites provide an exposed section through ocean crust, which is otherwise inaccessible to observation except through ocean drilling. Therefore, they have been a key source of information on the structure and formation of the ocean basins. They are also useful as indicators of the position of previous ocean basins in ancient collision zones, such as the Paleozoic (ca. 500–350 Ma) Caledonian–Appalachian orogen in Newfoundland. Although the major product of mid-ocean ridges is basalt and gabbro, mafic magma in large chambers can sometimes differentiate into plagiogranite or tonalite, which contains abundant zircon. Such samples were used by Dunning and Krogh (1985) to date ophiolites associated with the pre-Atlantic Iapetus Ocean. A more recent study by Rioux et al. (2012a) dated zircon from gabbro in the Oman–United Arab Emirates ophiolite at the level of ± 20 Ka and showed that magmatism lasted over the interval ca. 96.4–95.5 Ma, providing constraints on spreading rate. Zircon from gabbro dredged at actively spreading ocean crust in the East Pacific Rise was dated over the range 142–127 Ka with errors of ± 6 to ± 80 Ka (Rioux et al. 2012b), and in the Mid-Atlantic Ridge over the range 290–90 Ka with similar errors (Lissenburg et al. 2012). At this level of precision, the age spread within samples probably reflects the time scale of crystallization of the gabbro plutons.

Large Igneous Provinces and Continental Reconstruction

Although differentiated gabbros and gabbro pegmatite can contain zircon, the realization that baddeleyite (ZrO_2) is a widespread trace mineral in mafic intrusive rocks (Heaman and Lecheminant 1993) allowed more general application of U–Pb geochronology to mafic igneous rock. Application of baddeleyite dating continued to be relatively rare until Soderlund and Johansson (2002) developed an improved method for recovering tiny baddeleyite crystals on the Wilfley table (a shaking table routinely used to concentrate heavy minerals such as zircon from

rock powders). One of the earliest applications of baddeleyite geochronology is Krogh et al. (1987). Davis and Sutcliffe (1985) dated early mafic plutonism associated with the 1,100 Ma Midcontinent Rift (MCR) using both zircon and baddeleyite, which both occur in the same mafic sill.

Mafic rocks in the continental crust tend to be concentrated in Large Igneous Provinces (LIPs) that are thought to have been caused by rapid massive basaltic eruptions due to decompression melting of the mantle during the ascent of mantle plumes. In many cases these events led to continental breakup and the formation of new ocean basins. Continental flood basalts associated with such events in the Precambrian are often eroded away but leave the source channels through which the magma ascended exposed as giant radiating dyke swarms. Evidence suggests that emplacement of these swarms was rapid (1 Ma or less, Lecheminant and Heaman 1989), so they form markers whose paleomagnetic directions can be used to define a polar wander path for the drifting continents, provided that their ages are precisely known. The latest work is focused on using ages to identify fragments of the same dyke swarms on different continents that drifted apart sometime after emplacement of the swarms. Their orientation can be used as a “bar code” to help fit the continental fragments together into their pre-rift configuration (e.g., French and Heaman 2010; Nilsson et al. 2010; Soderlund et al. 2010).

Conclusions

The 60-year history of modern U–Pb geochronology of igneous rocks has produced an enormous amount of age data without which much of the progress in understanding ancient geological processes would not have been possible. Different methods of U–Pb dating (ID-TIMS, SIMS, LA-ICPMS) have been developed, but it is generally recognized that they have complementary strengths and weaknesses, so the best approach is to use them where they are most effective. Accuracy and sensitivity continue to improve with better instrumentation and understanding. It can be expected that sub-million-year age resolution will become available throughout the time scale, providing new insights into planetary development.

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Uranium-Lead, Ore Deposits

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Definition

Metamictization. Gradual to complete transformation of an originally crystalline mineral into the amorphous state by exposure of the crystal lattice to alpha particles emitted from U and Th.

$\mu. {}^{238}\text{U}/{}^{204}\text{Pb}$, atomic ratio.

Ore deposit. Natural occurrence of mineral(s) that can be worked at an economic profit, generally used for metallic minerals. The broader term *mineral deposit* also includes nonmetallic minerals.

Introduction

The first age determinations based on the radioactive decay of U were made on ore minerals, using the U-He method (1904) and the U-Pb chemical method (1907; see “► [Uranium-Lead, Chemical Isochron U-Pb Method \(CHIME\)](#)”). The first U-Pb isotopic ages and ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ages also were determined on ore minerals (see “► [Historical Development \(of Dating Methods\)](#)” and “► [Uranium-Lead Dating](#)”). This early interest in (uranium and uranium-rich) ore minerals for dating mainly was due to the large amounts of U, He, and Pb, respectively, needed to determine their contents – and, thus, He/U and Pb/U ratios – reliably. Nonetheless, these early age determinations were not precise. Furthermore, it became increasingly apparent that some of these ages also were inaccurate due to open-system behavior of the U-He and U-Pb systems in high U minerals. With the development of the K-Ar, Rb-Sr, and the ${}^{40}\text{Ar}$ - ${}^{39}\text{Ar}$ methods and later the Re-Os method (see “Ar-Ar and K-Ar Dating,” “Rb-Sr Dating,” and “Re-Os Dating”), direct dating of ore minerals by the U-Pb method was increasingly substituted. An exception to this trend represents the dating of U deposits, where U-Pb dating continued to be the method of choice. At the same time as the role of the U-Pb method lost importance in the dating of ore deposits, the U-Pb dating of – in particular – zircon, monazite, and xenotime evolved to become the most precise and accurate dating method for magmatic and metamorphic rocks (see “► [Uranium-Lead, Zircon](#)”).

The dating of gangue minerals (by K-Ar, Rb-Sr, and the ${}^{40}\text{Ar}$ - ${}^{39}\text{Ar}$ methods) or sulfides (Re-Os method) avoids some of the problems inherent to the dating of U-rich minerals by the U-Pb method (e.g., open-system behavior due to metamictization), but results in a series of other problems: (i) the dated gangue mineral and the ore minerals may be not cogenetic; (ii) the geochronologic system of some gangue minerals may be easily reset during later overprint (i.e., deformation, fluid flow, metamorphism), resulting in a system in which the dated mineral may be texturally related to the ore formation, but its age, however, corresponds to the overprint; (iii) the paragenetic redistribution

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of ore elements into secondary minerals may occur much later than the deposit formation and may not be related to the formation of dateable gangue minerals.

In the 1990s, U-Pb ID-TIMS dating of ore minerals regained importance, especially the dating of Nb-Ta minerals of the columbite-tantalite-tapiolite series and to a lesser extent Sn and W minerals (cassiterite, ferberite-hübnerite). Furthermore, the development of the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) U-Pb dating method provided a rapid and relatively cheap dating tool increasingly used to date ore minerals. Dating of ore minerals, as for instance columbite-tantalite or cassiterite, allows not only the dating of ore deposits and the linking of the ore deposits to a broader geological context but also the use the age of detrital grains from heavy mineral concentrates as a guide for exploration/prospection for the primary deposit and for the provenance certification of ore concentrates to suppress ore trading from areas of armed conflicts, e.g., COLTAN (http://www.bgr.bund.de/EN/Themen/Min_rohstoffe/CTC/Home/CTC_node_en.html).

With the development of microanalytical tools, such as high-resolution ion probes and LA-ICP-MS (see “► [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)”), minerals typically used for the dating of magmatic and metamorphic rocks by conventional isotope-dilution thermal ionization mass spectrometry (ID-TIMS), i.e., zircon, monazite, and xenotime, became increasingly used for the dating of ore deposits, in particular for hydrothermal ore deposits.

Direct Dating of Ore Deposits

Dating of ore minerals provides the most straightforward approach to date an ore deposit and to give insight into different stages of metal redistribution. Basically, any mineral can be dated by the U-Pb method if it fulfills the following constraints: (i) its composition allows for the substitution of U into the crystal lattice (e.g., U may substitute for Fe and Mn), (ii) the crystal lattice has no places for the substitution of Pb (Pb readily substitutes for K or Ca), and (iii) the mineral is chemically stable and is not easily altered. For U-Pb dating, it is not a high U content that is important, but a high $^{238}\text{U}/^{204}\text{Pb}$ ($= \mu$) ratio. Actually, minerals with high U contents tend to become metamict and, thus, open systems. In contrast, minerals with relatively low U content that effectively exclude the incorporation of Pb during their formation have high μ ratios, will not turn metamict, and eventually develop very radiogenic Pb isotopic composition. These minerals are suitable for U-Pb dating. It should be noted that minerals that can be dated by the U-Pb methods commonly are not major phases in the ore deposit (exception are U minerals in U deposits): if the available U is distributed among the major phases, none of them has a particularly high μ , which would make it unattractive for U-Pb dating.

A wide range of primary and secondary U minerals has been dated by the U-Pb method, yielding precise and accurate ages. Nonetheless, dating of U minerals is not trivial, and there is a plethora of processes (five are listed here) that may disturb the U-Pb systematics and result in both imprecise and inaccurate ages:

1. High U minerals produce with time significant amounts of Pb that may not be accommodated in the crystal lattice and form separate Pb phases (e.g., galena) with anomalously radiogenic Pb isotopic compositions. This results in a variable reduction of the apparent Pb/U ages of the U mineral.
2. Metamictization may lead to open-system behavior (see below).

3. Fine-grained U minerals may experience significant amount of intermediate daughter loss (see below).
4. Many U minerals are rather chemically reactive, and U (as U^{6+}) may be redistributed by oxidizing fluids. This redistribution commonly results in $^{238}U/^{234}U$ and $^{238}U/^{230}Th$ activity disequilibria, which for geologically young secondary minerals affect the U-Pb ages.
5. If secondary U minerals do not exclude Pb completely, they may incorporate highly radiogenic Pb from the precursor mineral.

Zircon, xenotime, and monazite from pegmatites, high-level granites, and greisen typically are very U or Th rich and commonly have variably disturbed U-Pb systems that do not allow for precise and accurate U-Pb dating of these rocks. Columbite-tantalite represents an alternative for dating these rocks (e.g., Romer and Smeds 1996). Although columbite-tantalite also may have high U contents, metamict sections can be removed by selective dissolution, which eventually yields concordant U-Pb data. Incomplete dissolution of metamict parts of the crystal commonly yields variably reverse discordant data and a negative lower intercept. Columbite-tantalite also has been successfully dated by LA-ICP-MS. In addition, cassiterite has been successfully dated by the U-Pb ID-TIMS method, but it has thus far not been used widely, possibly due to dissolution problems (Gulson and Jones 1992).

Carbonatites and related alkaline rocks have been successfully dated by U-Pb dating of perovskite and baddeleyite (see “► [Uranium-Lead, Rubidium-Strontium, Kimberlite](#)”). In contrast, zircon in carbonatites and related alkaline rocks may have been introduced during explosive emplacement to a significant extent from the wall rocks. Other minerals in these rocks that may be accessible to U-Pb dating include apatite and columbite-tantalite, whereas other Nb-Ta-rich minerals like euxenite, pyrochlore, and microlite commonly have higher U and/or Th contents and therefore become metamict over time, making them effectively unsuitable for U-Pb dating.

Indirect Dating of Ore Deposits

For many ore deposits, direct dating is not possible, either because the ore minerals cannot be dated (low U contents and high Pb contents) or because the datable minerals are rather easily altered or have such high U contents that they turn metamict and, thus, represent open systems for U-Pb dating. Indirect approaches to date ore deposits include (i) dating of non-ore minerals that are part of the same mineral assemblage as the ore minerals and (ii) dating of contact metamorphic minerals or selvages.

In Ca-silicate minerals, Pb generally substitutes to a significant amount for Ca, which results in low μ values for these minerals and significantly reduces their suitability for U-Pb dating. In skarn mineral assemblages, however, Pb typically is largely sequestered in calcite or epidote, leaving little Pb to be incorporated in other Ca-silicates. Therefore, skarn deposits have been successfully dated by the U-Pb method using a wide range of Ca-silicates, including garnet, vesuvianite, and titanite. In these minerals, U substitutes for Fe and may reach contents of a few ten to a few hundred ppm. As skarn minerals used for U-Pb dating may have relatively unradiogenic measured Pb isotopic compositions, the appropriate correction of initial Pb is very important, but not trivial as skarn minerals may contain initial Pb that is derived from both the intrusion and wall rocks and their relative contribution varied during the development of the skarn mineralization.

Magmatic iron ores have been successfully dated using titanite and apatite (Romer et al. 1994). Titanite intergrown with magnetite yields the emplacement age, whereas titanite in cavities yields

a minimum age for the emplacement of the iron ore. Apatite is considerably more readily disturbed than titanite and, therefore, should not be the mineral of choice for the dating of magmatic iron ores that have been thermally overprinted. Apatite may recrystallize at relatively low temperatures – in particular if a fluid is present – thereby losing some of its Pb, eventually yielding apparent ages that correspond to any point between the times of formation and disturbance. Furthermore, the rare earth elements (REE) in apatite may exsolve to form monazite (and less commonly xenotime), which also redistributes U, Th, and Pb between the host apatite and the secondary REE phosphates and, thus, disturbs the U-Pb system of apatite.

A wide range of minerals (e.g., apatite, zircon, titanite, monazite, xenotime, hübnerite) have been successfully used to U-Pb date hydrothermal vein deposits (Parrish 1990; Nesbitt et al. 1999; see also “► [Rubidium-Strontium, Hydrothermal Events](#)”). Especially if these minerals grow into open vugs, it is important to bear in mind that later fluid flow may result in partial resetting of their U-Pb system. Mineral growth from a fluid may result in strong fractionation of U and Pb, scavenging or incorporating U and leaving Pb in the fluid. Such minerals eventually develop highly radiogenic Pb isotopic compositions and may define precise ages. Calcite is a mineral that in rare occasions may be dated by the U-Pb method. Fe-Mn microparticles may scavenge U and develop radiogenic Pb isotopic compositions. The successful dating of such particles, however, depends on the presence of a container mineral that prevents intermediate daughter loss.

Magmatic and hydrothermal mineral deposits may develop marked contact metamorphic zones and selvages, respectively, that are accessible for isotopic dating. Thus, if there are no datable minerals in the magmatic or hydrothermal ore, such contact mineral assemblages may represent a last resort to constrain the age of the mineralization, as they commonly yield the maximum age for the mineralization.

Effects of Crystal Size and Metamictization

The decay of uranium (and thorium) to lead proceeds over a series of variably short-lived daughter isotopes. Each alpha decay results in the recoil of the daughter nucleus (see “► [Radiation Defect](#)”). This displacement leads to an open U-Pb (Th-U) geochronologic system on the nanoscale. As the U-Pb system of each small volume loses and gains daughter nuclei, this open-system behavior would become apparent at the nanoscale only if the distribution of U is heterogeneous. Otherwise, loss and gain are balanced. On the microscale, all recoil-related open-system processes effectively represent system internal redistributions of the daughter nuclei that do not affect the behavior of the bulk system; the U-Pb system appears as a closed system. In very small particles (10 μm or less), however, a significant portion of the recoiled nuclei is displaced to crystal surfaces and to linear and planar defects that favor the loss of intermediate daughter nuclei from the mineral. Among the intermediate daughter nuclei of the various U and Th decay series, ^{222}Rn and ^{226}Ra , which are intermediate daughters of the ^{238}U decay series, are especially likely to be lost. Radon is a gas and Ra is a water-soluble alkaline earth element that may substitute for Ba in silicates and sulfates. As ^{222}Rn and ^{226}Ra are longer lived than Rn and Ra isotopes of the ^{235}U and ^{232}Th decay series, it is only the ^{238}U - ^{206}Pb system of microcrystalline material that behaves as a notoriously open system. Although this open-system behavior affects all microcrystalline material, it becomes isotopically obvious especially in low-temperature U-rich rocks and ores, such as black shales, collapse-breccia pipes, and roll front-type uranium deposits that all may contain colloform and fine-dispersed uraninite. Consequences of the loss of intermediate daughter isotopes of the ^{238}U decay series are too-young apparent $^{206}\text{Pb}/^{238}\text{U}$ ages and too-old $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Nonetheless, in the

$^{235}\text{U}/^{207}\text{Pb}$ - $^{206}\text{Pb}/^{207}\text{Pb}$ diagram, the formation age may be derived for systems that had experienced combined Pb and Ra+Rn loss (Ludwig and Simmons 1991). Microcrystalline uraninite, however, may appear to have a closed U-Pb decay system if uraninite occurs as inclusions in another mineral that acts as container. Dating of the inclusion together with its surrounding container results in a closed U-Pb system that yields concordant data in the $^{206}\text{Pb}^*/^{238}\text{U}$ - $^{207}\text{Pb}^*/^{235}\text{U}$ diagram.

Alpha-recoil of the daughter nucleus results in lattice damage in the crystal. The tracks of the alpha particle and the daughter nucleus and – in particular – their stopping environments are volumes with broken crystal bonds. Although broken crystal bonds facilitate the migration of the daughter nucleus, each of these damaged zones is surrounded by crystalline material, effectively preventing migration and open-system behavior. It is the superposition of many of these damaged regions that results in increasingly larger volumes of damaged crystal lattice and longer transport distances. The damaged volumes eventually may intersect with linear (e.g., fission tracks) or planar (twin, deformation, and displacement planes) defects in the crystal or with crystal surfaces, allowing for open-system behavior of the U-Pb decay system (Romer 2003). The accumulation of defects, which results in the metamictization of the crystal lattice, depends on the uranium content of the mineral and time: the higher the uranium content, the sooner a mineral becomes metamict. The progressive metamictization of U-rich minerals is the reason why early dating attempts of ore minerals using the U-Pb system were not successful and why the U-Pb dating of old and/or U-rich minerals in general is problematic.

Effect of Multiple Metal Redistribution on U-Pb Dating

The structures that control the formation of ore deposits may be reactivated during later changes in the regional stress field, whereby metals of the existing ore deposit are redistributed. Similarly, metals of surface-near deposits may be redistributed by meteoric water. In both cases, this later redistribution may be the process that results in the concentration of the metal content to a level that makes it an economically interesting deposit. For these deposits, the age of formation of the primary deposit may be of less relevance than the age of enrichment. Metal redistributions are unlikely to be dated successfully by indirect methods. Direct dating using the U-Pb method may encounter two types of problems:

1. Secondary minerals that do not exclude Pb completely may inherit Pb from their precursor minerals. If the primary mineral had a high μ value, it would have developed a radiogenic Pb isotopic composition. Thus, such initial Pb would give the impression of the presence of an inherited component. In the concordia diagram, the U-Pb systematic of these secondary minerals would define a discordia line between the age of the secondary mineral and the age of its precursor mineral. If both primary and secondary deposits are relatively young, inheritance may not result in marked discordance and, instead, the data would define a data range of apparently concordant data.
2. In very young secondary minerals (a few 10^5 years) that can be dated by the U-Pb method, e.g., U-micas, the redistribution of U may be associated with an uncoupling of Th and U and thus in an initial disequilibrium in the ^{238}U - ^{206}Pb decay series (actually a deficit in ^{230}Th) that eventually results in a deficit in ^{206}Pb . Furthermore, there may have been an initial $^{238}\text{U}/^{234}\text{U}$ activity disequilibrium. Both of these disturbances can be accounted for.

Conclusions and Outlook

There is no fundamental difference between dating magmatic and metamorphic rocks and ore deposits by the U-Pb method. There are, however, a few problems that may be associated with the U-Pb dating of ore deposits that typically can be avoided for magmatic and metamorphic rocks. These include (1) open-system behavior due to metamictization (caused by high U contents), (2) intermediate daughter loss because of small crystal size, (3) multiple metal redistribution due to chemical reactivity of dated mineral (e.g., U minerals), and (4) unknown behavior of the dated mineral during thermal overprint and exposure to fluids. Some of these problems can be avoided by dating gangue minerals rather than the ore minerals.

The development of microanalytical in situ methods, in particular U-Pb dating by LA-ICP-MS, has significantly changed the possibilities in the dating of ore deposits. Most importantly, the ease and speed with which U-Pb LA-ICP-MS can be done allows a trial and error approach in minerals that have not yet been demonstrated to be reliable U-Pb chronometers. As positive as this extension of U-Pb dating to include uncommon ore minerals may appear, it is important to remember that all processes that lead to analytical problems in U-Pb dating by ID-TIMS, i.e., Pb-loss, metamictization, size-related loss of intermediate daughter isotopes, inheritance of radiogenic Pb from precursor minerals, and for very young minerals isotopic disequilibrium in the ^{238}U decay series, do not disappear only because U-Pb dating is done using a different analytical method. While these disturbances are readily apparent in precise and accurate ID-TIMS data – in particular minor Pb-loss and intermediate daughter loss – they may be analytically not resolvable in low-precision U-Pb data obtained by LA-ICP-MS or microprobe. The lack of resolution, however, does not a priori imply that these disturbances are not there. Furthermore, multiple events relatively close in time, which are analytically resolvable by U-Pb ID-TIMS, may yield overlapping U-Pb LA-ICP-MS data and thus, interpreted as a single event, result in apparently precise ages that are not accurate. Interpretation of such inaccurate data may lead to disturbed time scales for the development of ore deposits or to “processes” and “events” that actually do not exist.

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Historical Development \(of Dating Methods\)](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Radiation Defect](#)
- ▶ [Rb-Sr Dating](#)
- ▶ [Re-Os Dating](#)
- ▶ [Rubidium-Strontium, Hydrothermal Events](#)
- ▶ [Uranium-Lead Dating](#)
- ▶ [Uranium-Lead, Chemical Isochron U-Pb Method \(CHIME\)](#)
- ▶ [Uranium-Lead, Rubidium-Strontium, Kimberlites](#)
- ▶ [Uranium-Lead, Zircon](#)

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Uranium–Lead, Extraterrestrial, Early Solar System

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Synonyms

[Uranium–lead cosmochronology](#)

Definition

The science of relating events that transformed a cloud of interstellar gas to our solar system to time, by means of using decay of uranium isotopes ^{238}U and ^{235}U to lead isotopes ^{206}Pb and ^{207}Pb .

Introduction

Stars and their planetary systems form by gravitational collapse of dense parts in large interstellar molecular clouds. It is thought that, about 4.57 billion years ago, our solar system formed by a similar process. The early history of our solar system cannot be observed directly, but it is recorded in the very early minerals and rocks that were removed from the ongoing process of accretion before formation of the planets, and thus escaped geological reworking. These primitive rocks are preserved in several non-planetary environments – in asteroids that experienced only moderate heating, in comets – and as interplanetary dust particles floating in space. The asteroids that were extensively melted are thought to be the sources of igneous meteorites. Collisions between asteroids excavate rocks from their surfaces and interiors and, in some cases, send fragments (called meteoroids) to the Earth-crossing orbits. When meteoroids collide with the Earth's atmosphere, they get heated and produce glowing objects known as meteors (or shooting stars, or fireballs if larger than average size). Partial melting and ablation of the surface during atmosphere passage reduces the size of meteoroids and destroys many of them completely, but in many cases, their interior parts survive and fall on Earth. These remnants of meteoroids, known as meteorites, are our main source of knowledge about the chronology and evolution of our solar system.

Meteorites and Planetary Materials

The U–Pb-isotopic chronometer measures the timing of the last significant fractionation between U and Pb. Minerals and rocks that contain U, but did not incorporate any Pb during their formation, or lost all Pb in some secondary process, are most suitable for U–Pb dating and can produce the

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most accurate and model-independent ages. In terrestrial rocks and minerals, Pb is effectively excluded during crystallization of the minerals such as zircon from the magma. Along with high U concentrations about 10–1,000 ppm or higher, the absence of initially present Pb makes zircon, baddeleyite, and monazite the best geochronometer minerals. Magmatism in the Moon and Mars also produced zircon and baddeleyite, although not as ubiquitous as on the Earth due to the absence of abundant liquid water. These minerals are providing the most accurate U–Pb-isotopic dates for lunar (Nemchin et al. 2009; Grange et al. 2013) and Martian (Zhou et al. 2013) rocks. In contrast, chondrites (meteorites from asteroids that never melted) did not experience large-scale melting. Zircon in chondrites is very rare, small, and low U and has an uncertain, possibly metamorphic, origin. Its usefulness for U–Pb dating has been, so far, very limited. Almost all existing data on chondrite U–Pb chronology were obtained by analysis of two types of objects. The first is mm-sized (rarely cm-sized) compact aggregates of various shapes composed of Ca, Al, Ti-rich oxide, and silicate minerals such as spinel, hibonite, Ca, Ti-rich pyroxene, melilite, and anorthite called Ca, Al-rich inclusions, or CAIs. The second is mm-sized or smaller spherical aggregates composed mainly of ferromagnesian olivine and pyroxene with some feldspathic glassy or microcrystalline material (known as mesostasis) and less abundant Ca-rich pyroxene, Fe, Ni metal, and sulfides called chondrules. It is thought that chondrules formed through local flash heating of the nebular dust, with possible addition of earlier asteroidal melts in some cases. Most CAIs and chondrules experienced partial or complete melting, but because of their small size and rapid cooling, the melt differentiation did not do far enough to produce datable zircon and baddeleyite. However, small size of chondrules and CAIs, and relatively low pressure in the nebula where they formed, caused efficient Pb removal through evaporation. This fractionation, driven by the large difference in volatility between U and Pb (Lodders 2003), is the main geochemical mechanism that makes dating of the chondrite components possible. Achondrites occupy an intermediate position between chondrites and planetary materials. Their parent bodies have experienced both evaporation and magmatic differentiation. In some cases, one or both of these processes efficiently fractionated U and Pb, and such achondrites (e.g., angrites) are key materials in constructing the early solar system timescale.

The Early Days of Cosmochronology

The U–Pb cosmochronology was born in 1942–1946, when E. K. Gerling, A. Holmes, and F. G. Houtermans estimated the age of the Earth at 3.0–3.9 Ga on the basis of A. Nier's Pb-isotopic analyses of lead and uranium ores (see review by Mattinson 2013). In the mid-1950s, the U–Pb dating method was actively developed and applied to common geological problems by dating minerals such as zircon (Tilton et al. 1955). Cosmochronology was established as a quantitative scientific discipline as a part of that development and the desire to apply the improved dating methods to the most challenging problems. It is marked by the papers by Patterson (1955, 1956), where the ages of meteorites now known as equilibrated ordinary chondrites, eucrites, and iron meteorites were determined with the Pb–Pb method. The meteorite ages reported in these papers are often cited as examples of remarkable consistency with the current best estimate of the age of the solar system. Existence of short-lived radionuclides in the early solar system was discovered shortly after by Jeffery and Reynolds (1961), but for the following 30–40 years, the studies of the decay products of short-lived (now extinct) isotopes in meteorites were mainly concerned with nucleocosmochronology, understanding the history of stellar nucleosynthesis and the age of the elements (Podosek and Swindle 1988), while dating of solar system formation was based on the

same long-lived radionuclide systems that were used in terrestrial geochronology: U–Th–Pb, ^{40}K – ^{40}Ar , ^{87}Rb – ^{87}Sr , and ^{147}Sm – ^{143}Nd (Tilton 1988).

Modern U–Pb Among Other Meteorite Dating Methods

In the late 1980s and 1990s, it was realized that the duration of solar system formation was only of the order of 10 Ma and precision of about 1 Ma or better is required to resolve events. The short-lived chronometers can provide such precision, whereas the long-lived systems, with the exception of $^{207}\text{Pb}/^{206}\text{Pb}$, cannot. As a result, modern chronology of the earliest solids relies entirely of extinct radionuclides with half-lives shorter than ~ 20 Ma, coupled with the U–Pb system. The most popular extinct radionuclide chronometers, which are also most commonly used together with U–Pb, are ^{26}Al – ^{26}Mg (half-life 0.7 Ma), ^{53}Mn – ^{53}Cr (half-life 3.7 Ma), and ^{182}Hf – ^{182}W (half-life 8.9 Ma). While the other long-lived (extant) radionuclide pairs – ^{40}K – ^{40}Ar , ^{87}Rb – ^{87}Sr , ^{187}Re – ^{187}Os , ^{176}Lu – ^{176}Hf , ^{147}Sm – ^{143}Nd , and ^{146}Sm – ^{142}Nd – are very important as terrestrial and planetary chronometers, and isotopic tracers for both terrestrial and extraterrestrial rocks, their role in dating pre-planetary rocks is limited (Kleine and Rudge 2011; Amelin and Ireland 2013).

Methodology and Techniques of U–Pb Dating Meteorites

All U–Pb dates of meteorites with precision of better than 1–2 Ma, sufficient to resolve the timing of the stages of accretion, are obtained by analyses of either whole rocks or minerals such as clinopyroxene or Ca phosphates apatite and merrillite, after removal of the surface contamination containing non-radiogenic Pb by acid leaching. Both thermal ionization mass spectrometry (TIMS) and multicollector plasma ionization mass spectrometry (MC-ICPMS) are capable of producing very precise dates. Isotope dilution using ^{202}Pb – ^{205}Pb double spike for Pb and ^{233}U – ^{236}U double spike for U is becoming increasingly popular and is used with both TIMS and MC-ICPMS. Using double spikes is recognized as the most capable way for accurate determination of concentrations and isotopic compositions of Pb and U with simultaneous fractionation correction. Other techniques – standard-sample bracketing and fractionation correction relative to $^{203}\text{Tl}/^{205}\text{Tl}$ – can be used to precisely measure Pb-isotopic composition by MC-ICPMS, but they unfortunately cannot precisely measure U–Pb ratios in the same fraction. Since the discovery of significant $^{238}\text{U}/^{235}\text{U}$ isotopic variations in the CAIs (Brennecka et al. 2010), measurement of U isotopic composition is considered a mandatory part of every age determination of CAIs. Whether the same requirement applies to the studies of other meteorite components is currently unclear. Recent studies suggest that $^{238}\text{U}/^{235}\text{U}$ variations among chondrules, bulk chondrites, and achondrites are much smaller than in CAIs (Amelin et al. 2010; Brennecka and Wadhwa 2012; Connelly et al. 2012), even if they are slightly outside of the estimated analytical uncertainties. Using an average $^{238}\text{U}/^{235}\text{U} = 137.79 \pm 0.02$ in U–Pb dating of chondrules and achondrite is an acceptable temporary solution, but direct U isotopic analysis of every sample is a better approach.

Ages of CAIs

CAIs are present in most types of carbonaceous and ordinary chondrites, but only in CV (Vigarano type) carbonaceous chondrites, they are large enough to be extracted and dated individually

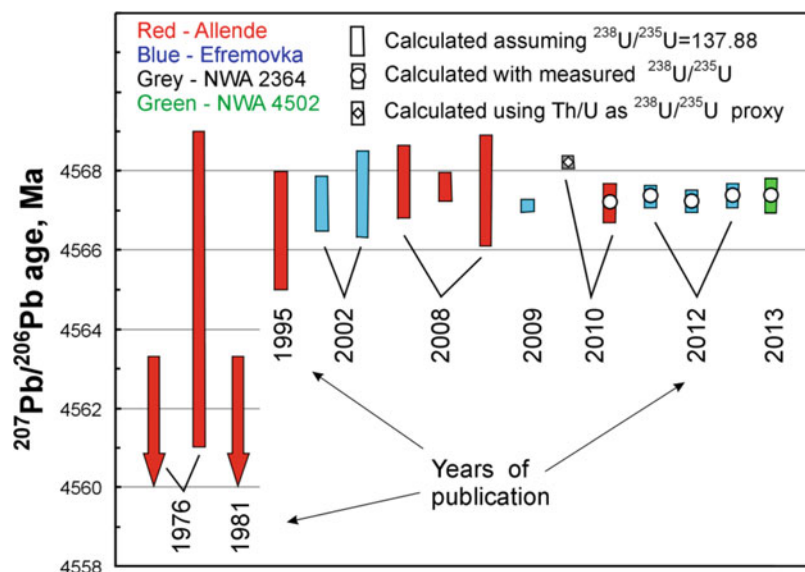


Fig. 1 Pb-isotopic ages of CAIs

(pooling several CAIs together to get more material is not acceptable because they are diverse in mineralogy and composition, even in a single meteorite). Ever since CAIs were recognized as the oldest macroscopic objects that formed in the solar protoplanetary disk, they attract attention of geochronologists and serve as the reference points in many timescales of the solar system formation. U–Pb ages of CAIs, from the first studies by Chen and Tilton (1976) and Tatsumoto et al. (1976), served as a time marker for the beginning of accretion in our solar system. Published Pb-isotopic ages of CAIs from CV chondrites, summarized by Tilton (1988), Allègre et al. (1995), Amelin et al. (2009), and recently by Amelin and Ireland (2013), are compiled in Fig. 1.

All CAIs studied between 1976 and 2002 were extracted from a single, very large, CV chondrite – Allende. Now precise Pb-isotopic ages are determined on the CAIs from four CV chondrites that differ in the degree of alteration in the parent body, shock, and terrestrial weathering. Despite this diversity in secondary processes, all recent age determinations of CAIs from Allende (Amelin et al. 2010), Efremovka (Connelly et al. 2012), and NWA 4502 (Amelin et al. 2013) are in excellent agreement, with a total range for the ages of about 0.2 million years – from 4567.18 ± 0.50 to 4567.40 ± 0.27 Ma. All these studies include analyses of the $^{238}\text{U}/^{235}\text{U}$ ratios. An attempt to calculate an age correction based on an empirical $^{238}\text{U}/^{235}\text{U}$ versus Th/U correlation for other CAIs produced a discrepant age for a CAI from CV chondrite NWA 2364 (Bouvier and Wadhwa 2010). This result further emphasizes that the $^{238}\text{U}/^{235}\text{U}$ must be determined in any chronological study of CAIs.

Ages of Chondrules

In Pb-isotopic dating of chondrules, it is more difficult to achieve high precision than in dating CAIs, because of lower U content (usually about 10–20 ppb), higher content of non-radiogenic Pb, and smaller size than CV chondrite CAIs. Like in dating CAIs, pooling several chondrules for analysis is undesirable, because ^{26}Al – ^{26}Mg ion microprobe dating of individual chondrules has revealed age variations between chondrules in most chondrites. Modern Pb-isotopic dates obtained on individual large chondrules from CR (Amelin et al. 2002) and LL3 (Connelly et al. 2012)

chondrites indicate that chondrule formation probably started simultaneously with CAI formation and continued for up to 3–4 million years. Several studies of chondrules from Allende, mostly using multi-chondrule fractions and/or older, less efficient leaching techniques, yielded similar although less precise ages. CB chondrites contain the youngest chondrules that postdate the CAIs by 4–5 million years (Krot et al. 2005). It was proposed that these chondrules, and metal grains – another main component of CB chondrites – formed from a vapor–melt plume produced by a giant impact between planetary embryos after dust in the protoplanetary disk had largely dissipated.

Ages of Achondrites

Eucrites – the most common stony igneous meteorites composed mainly of low-Ca orthopyroxene, plagioclase, and pigeonite, were among the first meteorites studied for U–Pb systematics. The eucrite Nuevo Laredo was analyzed by Patterson (1956) and provided the most radiogenic data point that largely controls the slope of the isochron he used to estimate the age of the solar system and the Earth. Eucrites remained popular in the studies of the early solar system chronology until the 1990s and helped to establish the main benchmarks of early solar system evolution. However, eventually it became clear that their complex geological history prevented accurate and straightforward age determination. Meteorites of other classes, such as angrites (basaltic achondrites composed of Al–Ca–Ti-rich clinopyroxene, Ca-rich plagioclase, and Ca-rich olivine), anomalous eucrite-like meteorites (coming from asteroids other than Vesta, which is thought to be the parent body of eucrites), and some unclassified basaltic achondrites, although rare, are better suited for high-resolution dating of the stages of nebular condensation and accretion. The oldest known achondrite is eucrite-like meteorite Asuka 881394 which is only 1–2 million years younger than CAIs (Wadhwa et al. 2009) and is approximately coeval with chondrules. Quenched angrites such as D’Orbigny, a subgroup of angrites with the texture indicating rapid cooling, postdate CAIs by 4 million years (Amelin 2008; Brennecka and Wadhwa 2012). Several anomalous achondrites with diverse mineralogy and chemical and oxygen isotope composition, indicating their origin from different asteroids, are 1–2 million years younger than quenched angrites (e.g., Bouvier et al. 2011). Plutonic angrites (a slowly cooled variety of angrites with similar mineralogy and oxygen isotopic composition as quenched angrites, and probably originating from the same asteroid) are 5–7 million years younger than quenched angrites. Eucrite-like achondrite Ibitira and primitive achondrite Acapulco (a rock with approximately chondritic composition but igneous texture, indicating melting of a chondritic source material with no igneous differentiation) have the same age as the youngest plutonic angrites, or about 10 million years younger than CAIs. These data indicate that many asteroids accreted and melted within 5–10 million years after the beginning of accretion marked by formation of CAIs and remained undisturbed since then. The 5–10-million-year time estimate is consistent with the estimated life spans of protoplanetary disks around young protostars based on astronomical observations.

Cooling History of Asteroids

Cooling paths of asteroids can be established by Pb-isotopic dating of two or more minerals from the same meteorite with different closure temperatures for diffusion of Pb (diffusion of U in the minerals used in U–Pb geochronology is much slower, so the closure of the isotopic system is

controlled by Pb diffusion). The cooling path deduced this way could be used to constrain the timing and duration of formation of the meteorite parent body and to interpret its structure. Some meteorites such as equilibrated (i.e., metamorphosed) ordinary chondrites and plutonic angrites contain U-bearing silicates and Ca phosphates apatite and merrillite that can be dated independently, and their ages interpreted as the timing of cessation of Pb diffusion in these minerals. Using experimental data on the rates of Pb diffusion in pyroxene and apatite of Cherniak et al. (1991) and Cherniak (2001) and Pb–Pb isochron dates of chondrules and apatite separates, Amelin et al. (2005) estimated the average cooling rate of the parent body of the Richardton ordinary chondrite (H5) at 26 ± 13 K/million years over the period of 4,563–4,551 million years. More precise Pb-isotopic dating of pyroxene and silicic apatite in the plutonic angrite NWA 4590 yielded the age difference of 0.55 ± 0.29 million years and a much faster cooling rate of 540 ± 290 K/million years, implying either a small size or a late breakup of the angrite parent asteroid.

Building Coherent Timescale of the Early Solar System with Integrated U–Pb and Extinct Radionuclide Dates

Although U–Pb is a versatile chronometer of meteorites, it can only date rocks and minerals that contain uranium, and events that fractionate uranium from lead. If a meteorite can be dated with one or more short-lived radionuclide chronometer, and it can be shown that these dates and the U–Pb date refer to the same event, then the extinct radionuclide chronometers can be linked to absolute time and a timescale of solar system formation can be constructed using multiple chronometers (see, e.g., Amelin and Ireland 2013 for details). This approach allows us to use minerals that concentrate short-lived radionuclides, such as plagioclase containing ^{26}Al , and olivine containing ^{53}Mn , as geochronometers, and date events that cannot be dated with the U–Pb method. A classical example is the timescale of the early solar system constructed by Lugmair and Shukolyukov (1998) using a set of ^{53}Mn – ^{53}Cr dates and the Pb-isotopic age of the angrite Lewis Cliff 86010 (Lugmair and Galer 1992) as an anchor to the absolute time. Angrites are especially well suited as reference samples for intercalibration of isotopic chronometers. Their rich and diverse mineralogy and good preservation of angrites enables their precise and accurate dating with many long-lived ($^{235,238}\text{U}$ – ^{232}Th – $^{206,207,208}\text{Pb}$, ^{176}Lu – ^{176}Hf , $^{146,147}\text{Sm}$ – $^{142,143}\text{Nd}$, initial Sr) and short-lived (^{53}Mn – ^{53}Cr , ^{26}Al – ^{26}Mg , ^{60}Fe – ^{60}Ni , ^{182}Hf – ^{182}W) isotopic chronometers. With multi-chronometer dates for several angrites and other well-preserved achondrites, as well as chondrules and CAIs, we can also verify initial abundances of short-lived radionuclides in the early solar system and find out whether they were homogeneously distributed. This information provides constraints on the environment in which our solar system formed, for example, it can tell us whether it was influenced by nearby massive stars during accretion.

Summary

The U–Pb system is a powerful and versatile chronometer of the early solar system materials and processes. Pb-isotopic dates show that CAIs formed 4567.2–4567.4 million years ago, chondrules formed during the following 3–4 million years, and differentiated asteroids formed between 1–2 and 10 million years after CAIs. This age distribution is consistent with an astronomical evidence on the rates of evolution of protoplanetary disks and suggests that, during accretion, our solar system comprised an assembly of hot and cold domains, pristine dust, and partially molten

planetesimals that coexisted and interacted for less than 10 million years. Subsequent metamorphic events and cooling of asteroids can be studied by Pb-isotopic dating of silicate and phosphate minerals from the same meteorite. Combining U–Pb with short-lived radionuclide chronometers helps to construct a timescale with higher resolution, tests it for internal consistency, and gives us hints to the environment of the solar system formation.

Cross-References

- ▶ [Extinct Radionuclide Dating](#)
- ▶ [Geochronology](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Meteorites \(Rb–Sr\)](#)
- ▶ [Meteorites \(Re–Os\)](#)
- ▶ [Meteorites \(Sm–Nd\)](#)
- ▶ [Meteorites \(U–Pb\)](#)
- ▶ [Meteorites \(Lu–Hf\)](#)
- ▶ [Thermal Ionization Mass Spectrometry \(TIMS\)](#)
- ▶ [Uranium–Lead Dating](#)
- ▶ [Uranium–Lead, Extraterrestrial, Planetary Materials](#)

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Apatite

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Synonyms

Chlorapatite (chlorine-rich variety); Dahllite (carbonate-bearing hydroxyapatite); Fluorapatite (fluorine-rich variety); Francolite (carbonate-rich variety); Hydroxyapatite (hydroxyl-rich variety)

Apatite is described herein and as a biomineral (biological apatite). The mineral apatite has the formula $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ and is characterized (Fig. 1) by phosphorus tetrahedrons which share oxygen with nine-coordinated calcium sites and singly charged anion lattice sites hosting F, Cl, or OH that are surrounded by a planar arrangement of three calcium atoms (Beever and McIntyre 1946). It occurs widely as an accessory mineral in all classes of rocks: igneous, metamorphic, and sedimentary (Klein and Hurlbut 1999). It is also found in pegmatites and other veins, probably of hydrothermal origin. The source of its datability is the radioactive trace element uranium that substitutes for calcium.

It is most commonly used as a dating material in thermochronology of large-scale earth processes via three different dating methods: (U-Th)/He, $^3\text{He}/^4\text{He}$, and fission track, recently covering topics such as exhumation studies of mountain ranges (Cecil et al. 2006), transient erosion of orogens (Rahl et al. 2007), glacial erosion (Ehlers et al. 2006; Shuster et al. 2005), and erosion of foreland basins (Cederbom et al. 2011) or exotic applications like the age and temperature of shock metamorphism

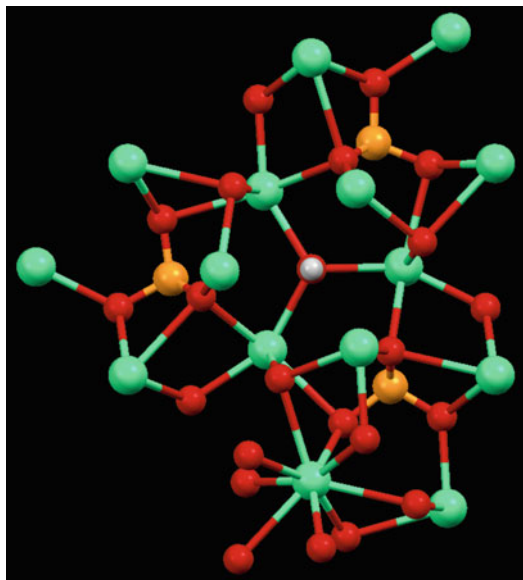


Fig. 1 Apatite structure viewed along the c-crystallographic axis: *green* = calcium, *red* = oxygen, *orange* = phosphorus, *white* = fluorine, chlorine, or hydroxyl

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of meteorites (Min et al. 2004). Apatite's versatility as a dating material is attested through the wide array of other dating methods that have been applied. Thomson et al. (2012) have reported the successful application U-Pb dating in apatite using laser ablation multicollector inductively coupled plasma mass spectrometry. In addition, cosmogenic nuclide dating of apatite using ^3He (Farley et al. 2006), uranium-series dating of phosphorites (Jarvis et al. 1994), and Lu-Hf and Pb step-leaching geochronology in metamorphic apatites have also been reported.

Cross-References

- ▶ [\$^3\text{He}/^4\text{He}\$](#)
- ▶ [Cosmogenic Nuclides](#)
- ▶ [Fission Track](#)
- ▶ [Thermochronology](#)
- ▶ [Uranium Lead](#)
- ▶ [Uranium-Series](#)

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Feldspar, Infrared-Stimulated Luminescence

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Definition

This entry primarily concerns the characteristics and the origins of infrared-stimulated luminescence in feldspars.

Introduction

Feldspar is a dominant (~60 %) rock-forming mineral group in the Earth's crust. Plagioclase feldspars ($\text{NaAlSi}_3\text{O}_8$ – $\text{CaAl}_2\text{Si}_2\text{O}_8$) are also commonly observed in meteorite samples and are a major mineral constituent on the surface of other extraterrestrial bodies such as the Moon and Mars. In luminescence dating, K-feldspar (KAlSi_3O_8) is the most commonly used dosimeter after quartz.

Feldspars have a direct band gap (with parabolic conduction/valence band) which varies with mineralogical composition: 7.86, 7.70, and 7.62 eV in $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , and $\text{CaAl}_2\text{Si}_2\text{O}_8$, respectively (Malins et al. 2004; Poolton et al. 2006). Additionally, feldspars have low-mobility band-tail states which may extend up to >1 eV in individual samples (Poolton et al. 2006, 2009). Both structural and atomic defects states occupy the band gap, which give feldspars their dosimetric (geochronometric) characteristics. Exposure to ionizing radiation creates free charge (electrons and holes) that can be trapped at these defects and be subsequently excited either thermally or optically in the UV–vis–NIR (ultraviolet–visible–near infrared) range. This entry concerns the near-infrared (NIR, henceforth IR) resonance feature observed between 750 and 1,000 nm during optical stimulation of these trapped charges and its dosimetric characteristics.

The main interest in the IR resonance in feldspars follows from the fact that IR-stimulated luminescence (IRSL) signal grows to typically more than 1 kGy with ionizing dose, thus giving the potential for increasing the upper end of the optically stimulated luminescence (OSL) dating range by a factor of about 5–10. Moreover, feldspar IRSL is typically the only preferable dating signal either in samples that lack quartz (e.g., basic volcanic provinces, Moon, Mars, meteorites, etc.) or in samples that have insensitive quartz. Being mineral specific, there is also a significant methodological value in using IR resonance for targeting, identifying, or cleaning signals from feldspar phases in untreated polymineral samples (e.g., fine silt or clay-sized sediments, or field dating samples).

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Historical Development

To the author's knowledge, the first published study demonstrating the phenomenon of OSL was based on IR stimulation of prior excited strontium sulfide and strontium selenide (rare earth element doped) phosphors (Ellickson 1946). Ellickson demonstrated that there is a relationship between the IRSL signal and the thermoluminescence (TL) traps in these materials and that the shape of the IRSL signal decay is dependent on the IR intensity and it followed second-order kinetics. However, it took several decades to realize the potential of OSL or IRSL in dosimetry and dating. IRSL was independently discovered by Hutt et al. (1988) while measuring excitation spectra of previously irradiated K-feldspar samples. These authors observed strong multiple, overlapping peaks in the region of 1.2–1.6 eV (~750–1,000 nm) and proposed that the IR resonance in feldspars arises by a two-step process: IR photon absorption by a trapped electron (photoionization energy of ~2.5 eV) causing transition to its excited state, followed by a thermally assisted transition to the conduction band. This study kick-started widespread use of feldspar IRSL for luminescence dating because of cheap availability IR light-emitting diodes (Poolton and Bailiff 1989) that could be easily implemented in a TL/OSL reader (Bøtter-Jensen et al. 1991). Subsequent studies established that IRSL was thermally stable and bleached easily with daylight, although somewhat less rapidly compared to the OSL of quartz (see Murray et al. 2012), making it a suitable signal for dating. However, unfortunately, IRSL signal suffered from a special type of instability popularly known as “anomalous fading” (loss of thermally stable charge at room temperature; Wintle 1973). In the last two decades or so, the single biggest issue in IRSL dating has been tackling the anomalous fading problem. For example, there has been focus on defining the mechanisms of fading (Spooner 1994; Visocekas et al. 1994; Huntley 2006; Larsen et al. 2009), fading correction methods (Huntley and Lamothe 2001; Kars et al. 2008), and a hunt for more stable IRSL signals (Fattahi and Stokes 2004; Tsukamoto et al. 2006; Thomsen et al. 2008; Buylaert et al. 2009, 2012; Jain and Ankjærgaard 2011). There has also been a significant thrust, both experimentally and theoretically, to understand the basic physical mechanisms involved in IRSL production with the ultimate objective of obtaining a better insight into the fading problem (e.g., Poolton et al. 1994, 1995a, b, 2002a, b, 2006; Jain and Ankjærgaard 2011; Andersen et al. 2012; Jain et al. 2012; Kitis and Pagonis 2013). See Duller (1997) for an extensive review on the subject.

Characteristics of the IRSL

The IRSL emission occurs in several different bands centered at ~1.7, 2.2, 3.1, 3.7, and 4.1 eV (see review by Krbetschek et al. 1997 and the later extensive survey by Baril and Huntley 2003a). Baril and Huntley observed for preheated samples that the 2.2 eV band was dominant in plagioclase feldspars, while the 3.1 eV band was dominant in alkali feldspars. They also observed a band at 1.7 eV that was primarily present in the samples that did not receive any preheating after irradiation. The 3.1 eV band is probably due to the native lattice defects, while 2.2 and 1.7 eV emissions are considered to arise from Mn^{2+} and Fe^{3+} transition metal ion impurities, respectively (see Poolton et al. 2001; Krbetschek et al. 1997). The 3.1 eV band is commonly used in IRSL dating, and it suffers from anomalous fading, which is now widely accepted to be caused by tunneling of electrons from the ground state of the dosimetric trap to the holes trapped at luminescence centers (Spooner 1994). It has been proposed that the orange-red emission in IRSL is more stable in terms of anomalous fading (Fattahi and Stokes 2004).

The UV band shows a strong thermal dependence at high temperatures (0.15 eV activation energy) and a small or no thermal dependence at low temperatures (0.05 eV–0.0005 eV activation energy) in both K- and Na-feldspar samples (Rieser et al. 1997; Poolton et al. 2009). It has also been shown that IRSL involves higher thermal activation energy at the end of the IRSL decay curve than at the beginning (Li 2010). The peak energy of the IR resonance is quite stable with temperature (Andersen et al. 2012); the main effect of temperature is an apparent broadening of the resonance structure. The IRSL decay rate generally increases with temperature (see McKeever et al. 1997); however, the extent of this change can vary significantly from sample to sample. An intriguing thermal characteristic of feldspar IRSL is that the net signal intensity as well as the net depletion of the trapped charge increases with stimulation temperature. Jain and Singhvi (2001) found that the dosimetric trap giving rise to OSL and IRSL in K-feldspar can be gradually emptied by high-temperature IR stimulations, suggesting a strong thermal dependence on trap emptying in the IRSL process. They attributed this effect to existence of a light sensitive trap deeper than the IRSL trap and speculated that this trap may not show anomalous fading because of expected greater localization. This thermal characteristic, general to all feldspars, implies that the IRSL signal can be regenerated thermally after IR bleaching at a lower temperature. For example, it is possible to do an IRSL measurement at room temperature followed by another measurement at a higher temperature (Thomsen et al. 2008) or by a sequence of systematically increasing temperatures (Li and Li 2011a); these signals are often known as elevated temperature “post-IR-IRSL” (pIR-IRSL) signals. The general characteristic of these high-temperature signals is that they show less anomalous fading compared to the first IRSL signal measured at room temperature (Thomsen et al. 2008; Li and Li 2011a; Buylaert et al. 2012).

Mechanism: IR Resonance and Luminescence Generation

The resonance feature observed in the excitation spectra of prior irradiated feldspar rock mineral or sediment samples has been widely studied by various workers (e.g., Bøtter-Jensen et al. 1994; Baril and Huntley 2003b; Poolton et al. 1995a, 1997, 2009; Barnett and Bailiff 1997; Andersen et al. 2012). The broad resonance spectrum consists of 1–3 overlapping peaks superimposed on a monotonously rising continuum. Spectral analysis suggests that there are two resonance peaks in the region ~1.42–1.56 eV, which are generally characteristic of most feldspar samples, and an occasional peak at about 1.25 or 1.34 eV.

The dominant resonance in the region of ~1.44 eV is widely accepted to arise due to ground-to-excited state transition in a deep dosimetric electron trap upon direct absorption of an IR photon and subsequent recombination. The exact peak energy of the resonance has been found to change with the feldspar composition. Poolton et al. (1995a) modeled this peak shift assuming a hydrogenic donor center (1s-2p transition) and an effective electron mass of $0.757 m_e$ to obtain peak energies of 1.44, 1.42, and 1.27 eV in K, Na, and Ca end-members, respectively. The effective electron mass was later confirmed to be $0.79 m_e$ using optically detected cyclotron resonance in a sample of Na-feldspar (Poolton et al. 2001).

Despite a general agreement on the origin of the resonant energy, there has been a considerable debate on the luminescence generating mechanism subsequent to resonant excitation. The Hütt model (Hütt et al. 1988) assumes recombination via the conduction band after a thermally activated transition from the excited state; however, the thermal barrier of about 0.8 eV for such a process is rather high and is not likely to be overcome on the measurement time scales (few tens of seconds) at or below room temperature. Studies using exo-electron emission have confirmed that the

conduction band does not participate in the IRSL process at room temperature (Ankjærgaard et al. 2006). The most widely accepted model today is the “band-tail state” model proposed by Poolton et al. (1994). These authors investigated the relationship between crystal structure and the OSL properties of feldspar and suggested existence of low-mobility band-tail states arising due to high density of atomic or structural perturbations (impurity atoms, variations in bonding angles, lattice distortions, etc.). The band-tail state model is based on a donor–acceptor recombination, where an excited state electron undergoes tunneling or phonon-assisted band-tail hopping in order to recombine with a trapped hole. This model also explains the broad continuum underlying the resonance peak (Poolton et al. 2002a, b).

The proof for the existence of the band-tail states and their role in charge transport by thermal hopping or tunneling comes in more recent studies (Poolton et al. 2009; Jain and Ankjærgaard 2011). Jain and Ankjærgaard (2011) developed a comprehensive phenomenological model based on a single dosimetric trap. They proposed that two dominant recombination routes in the band-tail states (0.05 eV phonon-assisted diffusion and quantum mechanical tunneling) together with energy-dependent, localized or delocalized recombinations give rise to a range of observable luminescence phenomena (both thermal and optical) in feldspars. This model is able to qualitatively relate all observable luminescence behavior of feldspar to a single dosimetric trap and the known available energy levels such as the excited state (~1.44 eV) of the trap and the band-tail states.

The IRSL Trap

There has also been a significant debate in literature on whether the IRSL signal originates from a single or multiple electron traps. The multiple trap hypothesis is generally based on examination of thermal characteristics of the IRSL signals; these include a systematic depletion in the TL signal with the duration of IR exposure (e.g., Duller 1995) and an increasing depletion in the IR intensity with preheat (anneal) temperature (the so-called “pulse-anneal” curves; Duller 1994). A gradual systematic decrease in such data, either as a function of exposure time or preheat temperature, suggests that IRSL arises from multiple discrete or a continuum of traps in feldspars. However, based on a systematic study of sample ages with preheat temperatures, Murray et al. (2009) concluded that decrease in the intensities of the low-temperature TL peaks due to IR exposure reflects reduction in the hole population rather than the trapped electron population. They identified the source of IRSL to be the trap responsible for the TL peak at ~400 °C. There has also been a significant discussion on the origin of the high-temperature or PIR-IRSL signals. Jain and Singhvi (2001) attributed that high-temperature IR stimulation accesses a deeper (type B in their terminology) trap compared to the IR at room temperature. They also speculated that the deeper trap may be more stable in terms of anomalous fading. The same hypothesis has been advocated also in later works to explain the pulse-anneal behavior of the PIR-IRSL signals (Li and Li 2011b). However, a consideration of localized recombination through the excited state in feldspars suggests that pulse-anneal curves can be explained by both single and multiple trap hypothesis and such data are, therefore, inconclusive for determining the types of trapping states (Thomsen et al. 2011). Jain and Ankjærgaard (2011) demonstrate that it is phenomenologically possible to explain all thermal and optical behavior of feldspars in terms of a single dosimetric electron trap with different recombination routes/mechanisms.

A more direct examination of the single vs. multiple trap issue is acquired through excitation spectroscopy. For a wide range of excitation energies (visible to IR), the luminescence output has

been observed to be consistent with a single trap model (Baril and Huntley 2003b; Andersen et al. 2012; Kars et al. 2013). Similarly, the resonance peak does not vary with stimulation temperature up to 290 °C apart from the expected thermal broadening effect suggesting that the same trap is sampled even at very high temperatures (Andersen et al. 2012). There has been observed a minor blue shift in the excitation spectra measured after a prior IR bleach (i.e., pIR-IRSL resonance) of about 10–20 meV; this shift is compatible with the measured phonon assistance required for electron transport in the band-tail states (Jain and Ankjærgaard 2011) confirming that IRSL and the PIR-IRSL signals arise from the same dosimetric trap (Andersen et al. 2012).

There have been several attempts to estimate thermal trap depth using the first-order analysis of the pulse-anneal data; these give a range of values: 1.7 eV (Murray et al. 2009), 1.66 eV (Li and Tso 1997), and 1.8 eV (Li and Li 2011b). The values for PIR-IRSL range from 2.2 to 2.4 eV or 1.9 to 2.1 eV depending on whether the continuum of states in the band tails is considered or not (Li and Li 2011b, 2013). It is, however, questionable whether the first-order analysis is valid for feldspars in view of the complex energy structure and different recombination routes (Jain and Ankjærgaard 2011). Jain et al. (2012) have developed a new numerical model for analysis of such systems, which seems to be able to explain the shape of the TL and IRSL decay curve using a single dosimetric trap (Kitis and Pagonis 2013). Further tests of the model to predict luminescence behavior of feldspars is necessary.

The presence of the band-tail states makes it difficult to measure the trap depth directly by optical methods. Some estimates of optical trap depth in literature are 2.5 eV (Clark and Sanderson 1994), >2.5 eV (Baril and Huntley 2003b), and >2.4 eV (Short 2005; Jain and Ankjærgaard 2011). In a recent extensive study, Kars et al. (2013) have given tentative estimates of optical trap depth to be ~2.1 for Na-feldspar and ~2.5 eV for K-feldspar.

Dating Methods Using IRSL

Use of IRSL in dating requires detection and, if necessary, correction for anomalous fading. Today the most commonly used dose measurement method is SAR (single-aliquot regenerative dose), which is based on sensitivity monitoring using a test dose (Murray and Wintle 2000; Wallinga et al. 2000). Estimation of precise fading rate for age correction has been an issue. Auclair et al. (2003) adapted the SAR method to measurement of fading rates, which are subsequently used to correct ages using a simple integration of charge depletion (t^{-1} dependence) and trapping over the geological time scales (Huntley and Lamothe 2001) or a more complex model using distance distributions (Kars et al. 2008). Age corrections are typically 20–40 % and the correction models are highly extrapolative. In the past 5 years, several new dating methods, based on very low or nonfading IRSL signals, have been proposed. Of these, the method based on the pIR-IRSL signals is becoming increasingly routine in dating applications; this method relies on preferential selection of electrons that are distant enough from any holes so as not to undergo ground-state tunneling in nature (Thomsen et al. 2008; Buylaert et al. 2012).

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Ancient Inks: A Forensic Art Historical Perspective

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Definition

Ink: A colored, usually liquid, material used for writing which is applied with a brush, stylus or pen to a variety of surfaces such as paper, papyrus, parchment, vellum or fabrics.

Inks have been used to record events and data in documentation and for the decorative arts since 2700 BCE; a description of the different types of ink used historically for nearly 5,000 years will be followed by a survey of analytical information available based on their chemical composition which can provide a chronological assessment. In conclusion, analytical case studies are presented briefly of two important historical manuscripts, namely, the *Vinland Map*, which purportedly was drawn in the early fifteenth century and shows the northeastern coast of North America some 60 years before the voyage of Columbus, and the Voynich Manuscript, a mysterious historiated fifteenth-century herbal which has thus far defied translation and which has been termed the most enigmatic ancient manuscript in existence.

Introduction

The earliest form of writing, cuneiform, involved the inscribing of characters into wet clay which was then fired to produce ceramic tablets; the adoption of cut reed pens and fluid inks applied to paper was perfected in China around 2700 BCE and attributed to the Chinese philosopher Tien-Lcheu. Hence, ink has existed for over 4,700 years of human history – its name derives from the Latin *incaustum* and the early French *encre*; a major problem in the dating of inked artifacts is the rather limited range of experimental compositions of historical inks, which can reliably be described as being either early carbon-based or later iron gallotannate inks (Thompson 1996; Cradock 2009; Brunelli and Crawford 2003).

The earliest ink, formulated in China from carbon black suspended in an aqueous solution of water and gum arabic, is now known as *India ink* because the best carbon supplies at that time for this purpose were sourced in India; the carbon was synthesized by burning wood such as pine, in which the partially combusted resin helped to bind the sooty deposits, in a limited amount of air under an upturned iron or ceramic dish. Other carbons were sourced from the calcination of animal bone and ivory, which produced a deeper black color – these contained residues of calcium phosphate derived from the hydroxyapatite component and provide an analytical signature of *bone black* or *ivory black*.

The discovery of natural mineral oils and petroleums afforded another opportunity for the production of a deep black sooty residue upon combustion in a limited supply of oxygen. A hierarchical basis for recipes for the production of carbonaceous soot existed in which certain botanical materials were highly prized for combustion to form the blackest inks, such as peach stones, almond shells, and vine twigs. There was much empiricism in the formulation of early inks

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as evidenced by the universal adoption of gum arabic as a binding agent; in addition to assisting the suspension of the insoluble carbon particles in the aqueous ink medium, the water-soluble gum arabic modified the viscosity of the ink, assisting in the writing flow when applied with reed pens, quills, and brushes and also improving the adhesion of the ink to the substrate. However, the addition of too much *gum arabic* resulted in a brittleness of the dried ink applied and a tendency for the writing to flake off – hence, the debris found between the leaves of ancient manuscripts frequently contains particles of ink from the associated script which can provide a rich source of analytical information without involving the destruction of the manuscript text. Different names have been recorded for carbon black inks through the ages, dependent upon formulation or source, such as *bistre* (Seaver 2004), an extract from sooty fires which possessed a warm brown color, and *sepia*, a dark, semitransparent ink from cuttlefish much used by the Romans.

Despite prior historical usage for a period of some 3,800 years, from about 1130 ACE *iron gall* ink replaced *carbon black* ink as the favored medium of writing; *iron gall* ink, more correctly described as an iron gallotannate, was the first water-based ink to be made from a chemical reaction between aqueous solutions of iron (II) sulfate and extracts of oak galls with the addition of gum arabic. Oak galls are spherical nutlike protuberances resulting from the egg laying of wasps on oak trees – the best galls were those fully developed from which the emerging wasp larvae had hatched. As encountered with the carbon-based inks, there are many recipes in existence for the manufacture of iron gall inks; indeed, the chronology for the first appearance of iron gall inks must predate the mediaeval since Pliny in the first century ACE describes in detail the preparation of aqueous gall solutions which blacken in the presence of *copperas*, an iron sulfate ore, which can be used for writing. An example of the complexity of an iron gall ink composition is provided by the following recipe for an ink “of the highest quality” in the sixteenth century: 8 oz powdered Aleppo galls, 4 oz logwood chips, 4 oz iron sulfate, 3 oz powdered gum arabic, 1 oz copper sulfate or verdigris (basic copper acetate), and 1 oz sugar – all heated and triturated in 12 lb of water followed by filtration and the addition of alum, ammonia, beer, lemon juice, oil of cloves, ground walnuts, lavender, wine, boiled oil, and extract of amber or shellac in brandy to minimize the growth of mould.

Iron gallotannate inks quickly became the medium of choice for mediaeval scribes because, unlike the carbon-based inks, they interacted chemically with cellulose substrates, conferring better adhesion and permanence on the script (Thompson 1956). However, this improvement in the better writing permanence of iron gall inks caused severe corrosion problems for paper manuscripts in particular. In some cases, this process resulted in the formation of holes in the manuscript (*lacunae*) in place of the writing (Fig. 1); many manuscripts have suffered irreversibly in this way and pose problems for conservation and the preservation of their integrity (Reissland and de Groot 1999; Reissland 2002). It has been found that arresting the decay can be achieved by the application of calcium bicarbonate, lime, magnesite, and calcium phytate, but generally irreparable damage has resulted for the original script and text (Rouchon-Quillet et al. 2004; Barrow 1972; Delage et al. 1990).

The corrosive effect of iron gallotannate inks upon cellulosic substrates can be related to the iron-catalyzed breakdown of cellulose in an acidic environment (Proost et al. 2004); in this process the Fe^{2+} react with acidic decomposition products of the cellulose to form hydroxyl and oxygenyl radicals, from which the subsequent creation of hydrogen peroxide destroys the cellulose substrate and oxidizes the iron to Fe^{3+} (Bulska and Wagner 2004). Hence, it has been suggested (Proost et al. 2004) that measurement of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in an ancient iron gall ink could provide a means of assessing its age, although clearly the actual rate of degradation of the ink would be dependent upon several environmental factors, not the least of which would be the recipe and formulation of the original ink. The elemental migration of iron atoms into the substrate also can

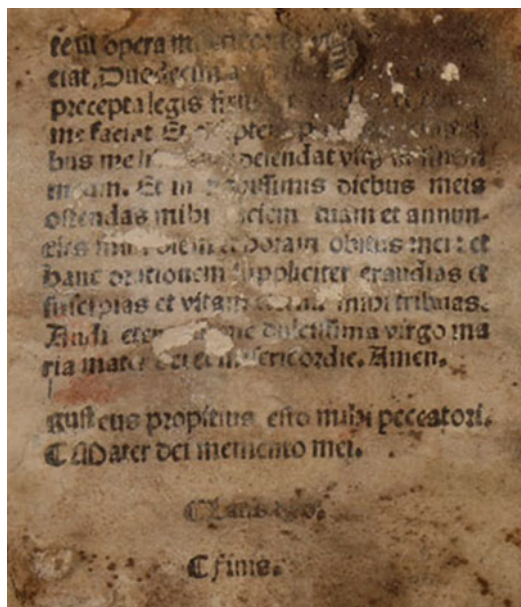


Fig. 1 A historical manuscript showing evidence of serious corrosive deterioration from iron gall ink on paper

provide a measure of the age of the script, as determined from Auger spectroscopy, but pitfalls can be encountered in the form of hair follicles in vellum substrates (de Pas and Flieder 1976).

The next development in ink manufacture occurred in the mid-nineteenth century, when a new range of organic dye-based colored inks became available following upon Perkin's synthesis of mauveine; at the London Society of Arts in 1858, the advent of this new range of brightly colored dyestuffs was advocated for ink manufacture with the additional adoption of graphite in place of soot for carbon-based inks.

Other Ancient Inks

It is true that most ancient manuscript texts and writing have been accomplished using black ink, but other colors have been identified, although these are strictly limited; examples include red inks (*cinnabar*, *dragon's blood*, *Brazilwood* extracts), purple (*folium*, *caput mortuum*, *purpurum* extracts) and gold. The major problem that was identified early on with the use of alternatives to carbon black or iron gall-based inks is that unless the pigment was a mineral, such as *cinnabar* or in some rarer cases *hematite*, the extracts from botanical or marine sources were dyestuffs, which were badly affected by light and handling – such was the case for *folium* (also known as *turnsole*) and *purpurum*. The ancient scribes and artists termed these dyes “fugitive” and thereby recognized their impermanence (Lee 2007; Ball 2001).

The problem that faces analytical scientists and art historians is the dating of inked manuscripts; unlike historiated manuscripts such as *Books of Hours* and the *Lindisfarne Gospels*, ancient texts and maps often do not have any coloring pigments associated with them, so the identification of the chemical composition of the ink was an important analytical source of information. Radiocarbon dating procedures are usually not practicable for the dating of ancient inks because of the quantities of specimen required in the destructive analysis, although of course some useful ancillary information can result from the radiocarbon dating of the manuscript substrates.

Dating of Ancient Inks

Traditional methods of characterization of ancient inks (de Pas and Flieder 1976; Cradock 2009) involve the application of techniques such as proton-induced X-ray emission (PIXE) spectroscopy, thin layer chromatography, ultraviolet–visible spectroscopy, infrared spectroscopy, Raman microscopy, micro-X-ray fluorescence spectroscopy, capillary electrophoresis, Rutherford back-scattering spectroscopy, scanning electron microscopy, scanning Auger spectroscopy, and mass spectrometry (La Porte and Stephens 2012; Senvaitiene et al. 2005). The major problems facing the analysts arise from variation of ink composition over the centuries. The central analytical discrimination for the differentiation between iron gall inks and carbon-based inks is the recognition of elemental carbon signals versus those of metallic iron. Secondary issues relate to the analytical identification of potential additives such as gum arabic, shellac, and copper; in this respect, infrared spectroscopy and mass spectrometry provide valuable molecular information that other techniques do not. Thin layer chromatography has been found to be not particularly useful for the compositional discrimination of ancient inks (Senvaitiene et al. 2005). In contrast, the identification of elemental iron by SEM/EDAXS, micro-XRF, and PIXE techniques is often used to indicate the presence of an iron gall ink in preference to a carbon-based ink. Iron gall inks possess an ultraviolet absorption with a sharp, strong band at 215 nm and a shoulder at 269 nm, characteristic of an iron gallotannate complex, compared with corresponding bands at 218 and 274 nm for the uncomplexed gallotannic acid.

Raman spectroscopy can be used to detect amorphous and graphitic carbon and has been applied to the analysis of ancient carbons and inks: a typical Raman spectrum of an ancient carbon derived from a botanical source gives two features, a broad band at $1,320\text{ cm}^{-1}$ ascribed to sp^3 hybridized carbon atoms (the D band) and a sharper band at $1,580\text{ cm}^{-1}$ attributed to sp^2 hybridized carbon atoms (the G band).

As an illustration of the information that can be deduced from the ink analysis of ancient manuscripts, two important manuscripts purporting to be from the fifteenth century will be described in more detail here – one of these, the *Vinland Map*, possesses only black ink on two sheets of vellum (Skelton et al. 1965; Seaver 2004), whereas the other, the *Voynich Manuscript*, is polychrome and comprises 240 sheets of vellum, but with again only black ink script (Kennedy and Churchill 2004; D’Imperio 2012). Both manuscripts were discovered in the early to mid-twentieth century with limited historical provenances and have since been the subject of some intense analytical eschatological and historical research.

Case Study 1: The Vinland Map

The *Vinland Map* is a vellum map of the Old World, measuring approximately $28 \times 40\text{ cm}$, that identifies an area in the Western Atlantic, *Vinlanda Insula*, the so-called Vinland of Scandinavian Viking folklore, showing an area to the northeast of North America, described thereon as “a new and fertile land to the west.” It first appeared in 1957 bound together with a manuscript known as the *Tartar Relation* (the *Historia Tartarorum*), which had an unusual composition of vellum and paper and two leaves of vellum alternating with six of paper, the latter exhibiting bulls’ head watermarks which were identifiable with the Basle Council of the 1430s. The cartographic importance of the *Vinland Map* centered upon its predating the voyage of Christopher Columbus and his epic discovery of the New World in 1492 by approximately 60 years and fed the rumor that

Columbus could actually have used such a map based on earlier Viking seafaring exploits, notably those of Leif Ericson (Seaver 1998).

In 1957, the *Vinland Map* and *Tartar Relation* were examined by British Museum experts in ancient maps and incunabula (Skelton et al. 1965). The philanthropist Paul Mellon donated them to the Beinecke Rare Book and Manuscript Library in Yale University, and in 1972 the Yale University Library commissioned an analysis of the *Vinland Map*, thereby starting a controversy which has raged for over 40 years and is still ongoing! The scientific analysis of the *Vinland Map* opened with a detailed polarized microscopic and X-ray diffraction (XRD) analysis of the inked areas (McCrone and McCrone 1974) from which it was concluded that the presence of anatase, a polymorphic form of titanium (II) oxide, in the ink dated the map firmly to the twentieth century (Gettens and Stout 1942) and indicating the *Vinland Map* to be a fake (Baynes-Cope 1974). Further analyses using scanning electron microscopy and energy-dispersive X-ray (EDX) (McCrone 1988; McCrone 1999) determined that the ink was not an iron gallotannate as found on the associated *Tartar Relation* but was carbon black. The ink and parchment of the *Vinland Map* were reanalyzed (Cahill et al. 1987) using proton-induced X-ray emission (PIXE) spectroscopy and challenged the McCrone conclusion (Delage et al. 1990). Radiocarbon dating of the vellum (Donahue et al. 2002) gave a date of 1432 $\pm$ 11 ACE, which agreed to within one standard deviation with the watermarked date on the associated paper in the *Tartar Relation*.

In 2002, a definitive Raman microspectroscopic study of the *Vinland Map* was undertaken (Brown and Clark 2002) with 632.8 nm laser excitation. The inked areas were apparently composed of two parts: a yellow line which was strongly adherent to the parchment substrate and an overlaid black line which showed evidence of severe loss in parts due to the black pigment “flaking off.” The analysis of the black ink gave the characteristic D and G bands for amorphous carbon at 1,325 and 1,580 cm^{-1} , respectively. The presence of anatase was evident, with characteristic bands at 142 and 398 cm^{-1} and seems to be indicative of a clever forgery; however, care must be taken as anatase has actually been identified in genuine archaeological artifacts significantly predating its established synthesis in the twentieth century (Edwards et al. 2006).

Case Study 2: The Voynich Manuscript

In 1912, Wilfrid Voynich revealed the discovery of his eponymous manuscript, which apparently dates to the early fifteenth century: the 240 vellum pages with black script and historiated polychrome figures, now labelled the “world’s most mysterious manuscript,” resemble a herbal compilation of botanical medicine and alchemy. Believed to be written either in a secret code or in a lost language, the major problem with this manuscript is that it has thus far defied all attempts at translation. The historical provenance of the *Voynich Manuscript*, like that of the *Vinland Map*, is steeped in international intrigue (Kennedy and Churchill 2004; D’Imperio 2012). A recent comprehensive and elegant analysis of the iron gall ink on the Voynich Manuscript has been undertaken (Barabe 2009) using polarized light microscopy, SEM/EDAX spectrometry, micro-XRD, and IR spectroscopy.

Unlike the *Vinland Map*, the *Voynich Manuscript* is historiated and has the advantage of supporting analytical information resulting from the interrogation of the associated pigments to assist in the chronology (Birren 1965; Feller 1966; Roy 1993; Fitzhugh 1997; Berrie 2007; Eastaugh et al. 2004; Harley 1982), which seems to be well established in the mediaeval period.

Conclusion

The identification of and analytical discrimination between ancient inks and the recognition of the corrosive nature of iron gallotannate inks are well documented, but the dating of specimen manuscripts is generally not feasible solely by examination of the ink composition alone; the consideration of associated information from radiocarbon dating of the manuscript substrates, eschatology, lexicography, and chronological placement of historiated pigments materially assists in the verification of the antiquity of a manuscript.

Cross-References

- [14C Dating](#)
- [Ink \(Modern\)](#)

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Volcanic Rocks, Ar/Ar

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Feasibility

The cooling rate for extrusive material (lava flows and ash beds) is rapid; even for lavas that are ~20 m thick, the central portions cool to <100 °C, in ~10 years following extrusion. Therefore, the time of emplacement is a geological instant as seen from the viewpoint of $^{40}\text{Ar}/^{39}\text{Ar}$ dating. It is critical that the material should remain “undisturbed” thereafter; the material should not be reheated to (say) >100 °C or suffer tectonic deformation. This is generally the case; exceptions are to be found in a series of lava flows (e.g., flood basalts) where reheating close to the contact with the overlying flow is to be expected. In collecting material for dating in such cases, samples must be taken from near the center of each flow, especially if the overlying flow is quite thick (> 10 m). In principle, any material containing measurable quantities of K should be datable; over 50 years of research has shown that the best materials for dating are the minerals sanidine, biotite, hornblende, plagioclase, as well as whole-rock material; for the latter, basaltic (mafic) material appears to be the best, though andesite and rhyolite have been dated successfully in whole-rock form.

Background

The $^{40}\text{Ar}/^{39}\text{Ar}$ method is the most widely used geochronological tool for volcanic rocks, capable of dating a wide variety of materials and covering the age span of ~2 ka to ~4.5 Ga (Renne et al. 1997; Renne 2000). It is particularly useful for dating of relatively young material (< 10 Ma) and yields high-precision ages. For older material where age comparison with other techniques (e.g., U-Pb dating) can be made, $^{40}\text{Ar}/^{39}\text{Ar}$ ages are very precise but commonly are ~1 % younger than U-Pb ages. Since the argon dating techniques are the only ones that utilize a gaseous substance as the daughter product, the possibility of partial resetting of the argon clock remains of concern. In $^{40}\text{Ar}/^{39}\text{Ar}$ stepheating, examination of the results on age spectrum/isochron plots was thought to overcome these problems. All plateau/isochron ages must pass the requisite statistical test for reliability (see Baksi 2005; Sharp and Clague 2006; Baksi 2010a). Further, the samples should be deemed to be unaltered as evaluated by the alteration index (AI) technique (Baksi 2007a), which looks to the level of $^{36}\text{Ar}_\text{I}$ in the phases that are being dated. This is critical, as numerous examples are seen in the literature in which statistically reliable plateau ages are known to underestimate the time of crystallization (Baksi 2010a, b, 2012a, 2014). The AI method works best for whole-rock mafic material as well as plagioclase (see Baksi 2010a, Fig. 2, and Baksi 2014, Fig. 8). Total gas or total fusion ages should not be unequivocally treated as accurate estimates of the time of crystallization (see Baksi 2012a, 2013).

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Mafic/Intermediate Lava Flows

These are normally dated using crushed whole-rock material and/or plagioclase separates. In both instances, the material used for dating must be as unaltered as possible. This necessitates handpicking of grains under binocular microscope, followed by acid leaching to remove altered phases. For whole-rock material, leaching with dilute nitric acid or hydrochloric acid is followed by washing with distilled/deionized water and dried. For plagioclase separates, leaching with dilute hydrofluoric acid, followed by careful rinsing and drying as above, is the best procedure. Whole-rock material often contains an order of magnitude more K than plagioclase and is easier to date from the analytical point of view, entailing use of smaller subsamples. However, the resulting age spectra commonly show the effects of ^{39}Ar recoil loss/redistribution, from fine-grained phases. Interpretation of such age spectra can be complicated, but with care, useful results can be recovered relating to the time of crystallization. Firstly, step age errors must be calculated carefully using methods set out in Dalrymple et al. (1981). In general, steps extracted at laboratory temperatures of $\sim 700\text{--}1,000\text{ }^{\circ}\text{C}$ may serve to define plateau sections; the highest-temperature steps (with high Ca/K ratios) are dominated by gas extracted from plagioclase (and less so from pyroxene) within the rock. Thus, a small(er) number of steps, each of quite high internal precision, may yield a plateau age. For plagioclase samples, recoil problems are generally absent; the purity and homogeneity of the subsample can be investigated by noting the $^{37}\text{Ar}_{\text{Ca}}/^{39}\text{Ar}_{\text{K}}$ (and hence the Ca/K) of each step in the age spectrum. Published age spectra for both whole-rock material and plagioclase should show the Ca/K ratio of each step. For unaltered plagioclase samples, it may be possible to obtain a plateau from (a larger number of) steps covering a wide range of temperatures ($\sim 600\text{--}1,400\text{ }^{\circ}\text{C}$), each of somewhat lower internal precision. The results should also be carefully examined on an isochron plot (preferably the inverse mode, $^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}$ versus $^{36}\text{Ar}_{\text{I}}/^{40}\text{Ar}$). If the resulting initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratio (IR) is statistically different from the atmospheric argon value (295.5), the plateau age should not be utilized. If the IR is >295.5 , the specimen displays the presence of excess ^{40}Ar , and the isochron age should be henceforward used. However, if the IR is <295.5 , the sample is disturbed (generally caused by alteration), and both the resulting isochron and plateau ages should not be used as accurate estimates of the time of crystallization.

Some important events dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique involve the rapid extrusion of large amounts of mafic rocks in flood basalt provinces. One example is the Parana flood basalts (South America) involving $\sim 1.5 \times 10^6\text{ km}^3$ of material erupted in $<1\text{ Ma}$ at $\sim 134\text{ Ma}$ (Renne et al. 1992). For younger flood basalt provinces, such as the Columbia River basalts in the USA, high-precision $^{40}\text{Ar}/^{39}\text{Ar}$ ages together with their magnetostratigraphy can be combined with the GPTS at $\sim 17\text{--}15\text{ Ma}$, to arrive at a more detailed history of eruption rates for this smaller ($\sim 1.4 \times 10^5\text{ km}^3$) flood basalt province (Jarboe et al. 2010; Baksi 2013).

Acidic Lavas and Ash Beds

These are best dated using sanidine separates. This high-K (8–14 %) mineral should be pure and unaltered. The latter involves binocular examination and picking, followed by washing with dilute HF as outlined above for plagioclase. Since sanidine is difficult to degas, a laser or double-walled vacuum apparatus (Staudacher furnace) should be used. Relatively small subsamples can be used and often show essentially flat age spectra, yielding high-precision plateau ages. Correction for $^{36}\text{Ar}_{\text{Ca}}$ is generally very small; care should be exercised in dealing with steps where the analytical data suggest that the $^{40}\text{Ar}^*$ content is $>100\text{ }\%$. In such instances, the step age should be corrected to

denote 100.0 % of $^{40}\text{Ar}^*$ (Baksi 2012b). If this procedure is not followed, the resulting (plateau) age is biased to the high (too old) side by an amount that may exceed the (2σ) internal error of the plateau age. The data should also be examined on isochron plots as outlined above. In many instances, the data points will fall close to the $^{39}\text{Ar}_K/^{40}\text{Ar}$ axis and the resulting isochrons will yield IR with large errors. Unless these values are statistically different from the atmospheric argon value, the plateau age and error should be used henceforward. In a limited number of cases, the IR will prove to be >295.5 , showing that excess argon is present. In this situation, the isochron age and error are to be used; an important case illustrating this is the work of Renne et al. (1997) in dating material from 79 AD eruption of Mt. Vesuvius.

Other materials from volcanic rocks that may be dated are micas (notably biotite) and amphibole (hornblende). In principle, biotite can yield high-precision results, but may be affected by three different sets of problems: (1) ^{39}Ar recoil loss from very fine-grained material, (2) the presence of excess argon, and (3) the purity of the material dated. The first of these would be indicated by total gas and/or plateau ages that are too old on stratigraphic grounds or compared to other dating methods; a check with the K-Ar date on the material can be useful. The presence of excess argon is often difficult to detect and correct, even for quite old material. This is best illustrated by the careful work of Renne (1995) in looking at material related to the formation of the Siberian Traps, USSR. This involved painstaking work on a number of biotite subsamples and comparison of the results with that obtained on coexisting hornblende; this source of error is evidently more serious for intrusive rocks, but may affect volcanic material also. The purity of the material dated can be checked by careful attention to the Ca/K ratio of each step. If these show values of >0.05 , the subsample may be chloritized to a degree that negates the use of resulting plateau/isochron ages. The use of amphibole separates to obtain accurate ages for volcanic material is relatively uncommon; due to the relatively low precision of ages (low K content) and seeming heterogeneity of “pure” separates, its utility will not be considered herein.

The melting of surface rocks by bolide impacts can be successfully dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, as evidenced by the work of Swisher et al. (1992) on the Chicxulub Crater (Mexico) thought to have been genetically linked to the global faunal extinction event noted at the Cretaceous-Paleogene boundary at ~ 65 Ma. In the age range of a few ka to few Ma, the $^{40}\text{Ar}/^{39}\text{Ar}$ step heating technique appears to yield good results.

Important Events Dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method

This method is the only parent-daughter geochronological system that yields high-precision results for young (< 10 Ma) rocks. For older material, the U-Pb methods when applicable yield ages that are more precise, are tied to absolute calibration of spikes, and are more “robust.” Two important (sets of) events of geological importance dated by the argon techniques are (1) the calibration of the geomagnetic polarity time scale (GPTS) for ~ 0 – 10 Ma and (2) the ages of rocks from the Hawaiian-Emperor Chain in the Pacific Ocean and the timing of the bend in the chain (HEB).

(1) The K-Ar-derived GPTS for 0 – 10 Ma, used to calculate seafloor spreading rates for many decades, was shown to have systematic errors, with “ages” that were ~ 5 – 7 % too young (Baksi 1995). Use of $^{40}\text{Ar}/^{39}\text{Ar}$ ages helped to illustrate that seafloor spreading rates calculated for the past ~ 3 Ma by geochronology, astrochronology (based on Milankovitch cyclicities), and space geodesy agreed to within ± 1 % (Baksi 1994). The errors in the K-Ar dates were caused by incomplete degassing of sanidine samples and/or alteration of whole-rock basalts, leading to lowered ages. In effect, alteration (chemical weathering) is ubiquitous and is best detected by noting the amount of

^{36}Ar released in each step of $^{40}\text{Ar}/^{39}\text{Ar}$ incremental heating studies (Baksi 2007a). (2) Since alteration is primarily caused by the interaction of silicate phases in rocks with water, submarine samples are commonly altered (Baksi 2007b). This is also verified by the work of Sharp and Clague (2006) who showed that the age of the HEB is 50 Ma – not the ~43 Ma previously used for three decades; critical examination (Baksi 2010b) reveals that the younger age (~43 Ma) is based on the dating of altered samples.

$^{40}\text{Ar}/^{39}\text{Ar}$ dating of young rocks/events is liable to be affected by the presence of small amounts of excess ^{40}Ar ; if uncorrected for, this can result in “ages” that are up to ~10 % too old. The dating of volcanic events took a leap forward through the work of Renne et al. (1997), who obtained the correct age for samples erupted during the 79 AD eruption of Mt. Vesuvius. This calibration into the “historic realm” was achieved on sanidine which contained traces of excess ^{40}Ar . Careful examination of such data sets by the isochron technique (York 1969) is a critical component. Very young (< 300 ka) andesitic rocks from South America have been successfully dated in whole-rock form (Singer et al. 2008) and contain low level of $^{36}\text{Ar}_\text{I}$ (Baksi 2010b).

Problems Requiring Attention

For older material (> 50 Ma), $^{40}\text{Ar}/^{39}\text{Ar}$ ages tend to be ~1 % younger than (more robust) U-Pb ages (see Min et al. 2000; Baksi 2014). This systematic difference is thought to be caused by (a) incorrect choice (use) of the decay constants of ^{40}K and/or (b) incorrect (K-Ar) ages used for the monitors/standards utilized in $^{40}\text{Ar}/^{39}\text{Ar}$ dating work (see Renne et al. 2010). Making the necessary corrections to bring U-Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ ages into concordance for events >50 Ma (see Renne et al. 2010) results in systematic discordance in the ages for the GPTS (0–10 Ma) obtained by the $^{40}\text{Ar}/^{39}\text{Ar}$ method versus astrochronology (Baksi 2013). A careful *absolute* $^{40}\text{Ar}^*$ calibration of a commonly used mineral (standard) should have high priority. Currently, for the widely used Fish Canyon sanidine, the age is tied to the absolute age of GA-1550 biotite (see Renne et al. 1998). However, the argon calibration of GA-1550 biotite (McDougall and Wellman 2011) was achieved with atmospheric (air) argon that was not *dry*.

A final note of caution is made regarding the fact that radiometric ages for volcanic units must always fall in stratigraphic order, i.e., obey the principle of superposition. Numerous cases in the recent literature highlight problems that may occur in this regard (e.g., Barry et al. 2010, 2013; Baksi 2012a, 2013).

Cross-References

- ▶ [Ar-Ar and K-Ar Dating](#)
- ▶ [Biostratigraphy](#)
- ▶ [Chemical Weathering Indices](#)
- ▶ [Feldspar](#)
- ▶ [Geochronology](#)
- ▶ [Geological Time Scale](#)
- ▶ [Geomagnetism](#)
- ▶ [Historical Development \(of Dating Methods\)](#)
- ▶ [Magnetic Chronology](#)
- ▶ [Magnetostatigraphic Dating](#)

- [Mass Spectrometry](#)
- [Milankovitch Cycles](#)
- [Noble Gas Mass Spectrometer](#)
- [Principle of Superposition](#)
- [Single-Crystal Laser fusion](#)
- [Tephrochronology](#)
- [Uranium-Lead Dating](#)
- [Uranium-Lead, Igneous Rocks](#)
- [Uranium-Lead, Zircon](#)
- [Volcanic Rocks \(K-Ar and Ar-Ar\)](#)

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Chert

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Cherts are nodular masses and beds of microcrystalline quartz that replace carbonate sediment or opaline biologic oozes of diatoms or radiolarians during burial. The replacement can occur during early to deep burial, so chert is younger than the time of host sediment deposition by variable amounts not easily determined. The quartz itself contains no radionuclides that can be used for age-dating the time of crystallization. Detrital impurity grains may contain datable material, but the age is that of the source area and not of the sediment. The value of cherts in age-dating relates to the unsurpassed preservation that silicification affords fossils.

Silicification involves a slow micron-by-micron replacement process. Silicified fossils better survive the alteration effects of subsequent burial, uplift, and weathering. Acid dissolution of carbonate frees isolated examples, and these probably represent the majority of invertebrate fossils used to establish the paleontological record and to age-date sedimentary rocks. Ages established from the fossils relate to the time of original deposition even though silicification is secondary. Organic remains in nodular cherts can be preserved down even to the cellular level. Microfossils in such cherts provide much of the record of the Precambrian life, but their evolutionary history is still insufficiently established to be widely useful for age-dating.

In Cenozoic and Paleozoic bedded cherts, microquartz in the tiny volumes originally occupied by radiolarian tests resist dissolution in HF and NaOH relative to the matrix microquartz. Gentle etching reveals the radiolarian morphology so well that biostratigraphic ages can be established with surprising precision. Radiolarian age-dating of bedded chert sequences was a breakthrough in unraveling the structural geology and history of the great folded mountain sequences in the Alps and Western United States (e.g., De Wever et al. 2001). Tertiary diatomaceous oozes are abundant and incompletely transformed into microquartz. Fossil ages can be determined from these usually without acid etching.

The $^{18}\text{O}/^{16}\text{O}$ ratio of cherts is highly variable but generally decreases in progressively older cherts (Knauth 2005). The explanation remains controversial but is likely due to past higher climatic temperatures. The highest values for Archean examples are lower than the lowest values for younger examples, so the $^{18}\text{O}/^{16}\text{O}$ ratio is a crude age indicator of cherts older than 2.5 billion years.

Dissolved argon in the silicifying fluid can be trapped within tiny fluid inclusions in the microquartz that precipitates from it. Since the isotopic composition of atmospheric Ar evolves with time, appropriate samples might yield approximate age dates. Analyses of 3.5 billion-year-old hydrothermal quartz have now better constrained atmospheric Ar isotopic evolution, so this method holds considerable promise (Pujol et al. 2013).

While the geochemical and radiometric age-dating of cherts remains limited, biostratigraphic ages of the enclosed fossils remain among the most accurate achieved for the Phanerozoic

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sedimentary rocks. The exquisite microfossil record in older cherts, the “amber of the Precambrian,” offers hope for similar utility extending back in time to the earliest sediments.

Cross-References

- ▶ [Biostratigraphy](#)
- ▶ [Geological Timescale](#)

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Hominid Evolution Timescale

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The hominid evolution timescale has been established thanks to primate genomic sequencing (Schrager and Voloch 2013). It is now generally accepted that the divergence between our closest relatives, bonobos and chimpanzees (*Pan lineage*), and modern humans dates back to at least 7.0 Ma (Fig. 1) based on genetic data from extant primate species. However, discoveries of fossil hominins have also been crucial to the debate on the theoretical aspects and for the acceptance of the timing of the appearance of the hominin lineage. These fossils are still debated, but *Sahelanthropus tchadensis*, ca. 7 Ma, and *Orrorin tugenensis*, ca. 6 Ma, may represent one of the earliest evidences of the hominin lineage. Unfortunately, contemporary evidence of early specimens of the *Pan* lineage is not yet documented. The oldest fossils attributed to *Pan* are only 500 Ka and the divergence between bonobos (*Pan paniscus*) and chimpanzees (*Pan troglodytes*) would have occurred around 2 Ma based on genetic evidence. A discussion exists on the use of the terms hominid and hominin, but the general agreement, now, is to use the term hominin to refer to all the member of the human clade, i.e., to specimens that are bipedal and that share anatomical specificities related to this mode of locomotion. Between 6 Ma and 1.8 Ma, more fossil hominins are known. They belong to at least three genera (*Ardipithecus*, *Australopithecus*, and *Paranthropus* and maybe *Kenyanthropus*) and 13 species and were mostly unearthed in South and East Africa but also in Central Africa (Chad for *Sahelanthropus tchadensis* and *Australopithecus bahrelghazali*). Another major event on the hominid timeline was the appearance of the genus *Homo* around 2.5–2 Ma that coincides with the first hominin migration out of Africa. However, the definition of the genus *Homo* is controversial or at least problematic, as its ranges of anatomical and behavioral variations have been widely expanded and encompass those now known for other hominins. An important event of divergence between several species (*Homo heidelbergensis* and possibly *Homo rhodesiensis* emerging from *Homo erectus sensu lato* and then evolving into *Homo neanderthalensis* and *sapiens*) has occurred in Africa and possibly in Eurasia around 500 ka. That led in particular to the appearance of the *Homo sapiens* species 200 ka years ago. *Homo neanderthalensis* is important for cultural and historical reasons (first discovery of fossil hominin in Europe, questions on a possible other humanity, etc.), but also because it is the species with the largest fossil record in relation to their early use of burials. Finally, our species has cohabited with several other species (at least *Homo erectus*, *Homo neanderthalensis*, and *Homo floresiensis*) until very recent times, only several ka compared to 7 Ma of hominid evolution. Recent developments in paleogenetics (e.g., Meyer et al. 2012) have offered new information about the recent history of the human lineage, but these data need to be integrated in the wider range of existing paleoanthropological data (Henke and Tattersall 2007) to be interpreted.

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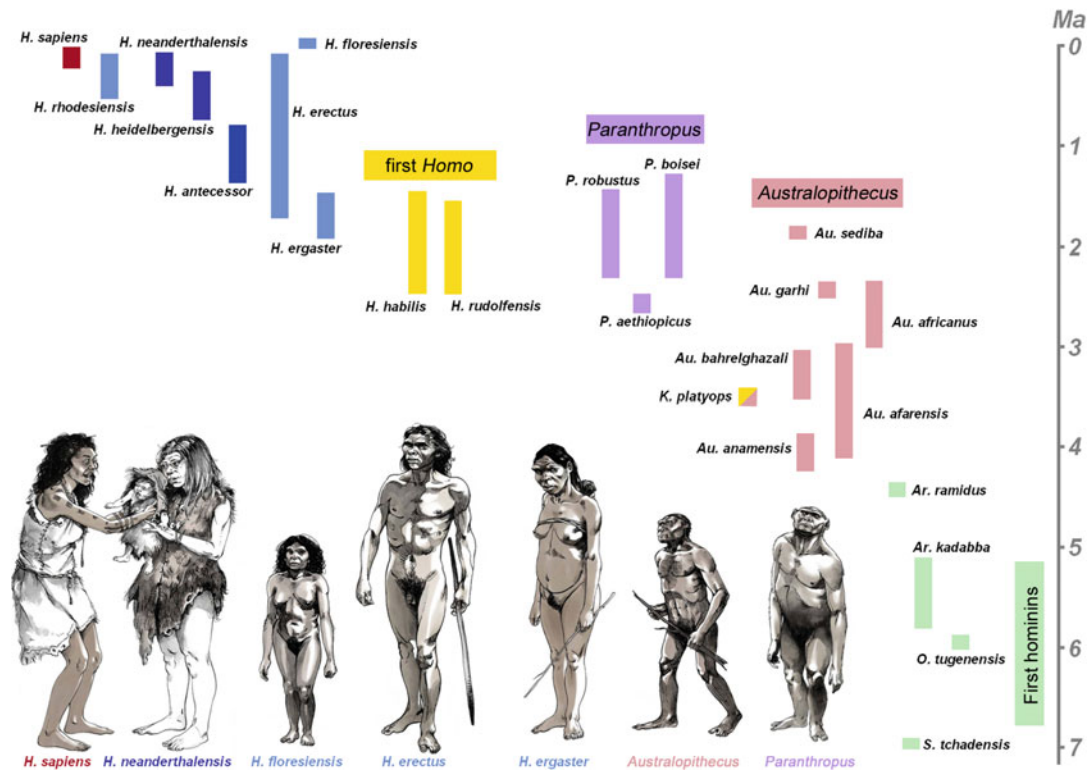


Fig. 1 Chronological distribution of hominin species and representation of selected species

Cross-References

- [Human Evolution \(Molecular Clocks\)](#)
- [Luminescence, Dispersion of Early Modern Humans](#)
- [Molecular Clocks](#)
- [Skeletal Remains \(14C\)](#)
- [Teeth \(ESR/U-Series\)](#)

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Lucy

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Lucy is the colloquial name given to a presumed female partial skeleton of the Pliocene hominin species *Australopithecus afarensis*. The specimen, cataloged as Afar Locality (A.L.) 288–1, was found by Donald Johanson in November 1974, at the Hadar site, in the west-central part of the Afar Rift Valley, Ethiopia. Pyroclastic sediments in the Hadar Formation at the Hadar site have been dated by K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods to between 3.4 Ma and 3.0 Ma, which brackets the younger half of the known temporal range of *A. afarensis* (Kimbel and Delezene 2009). More than 375 specimens of *A. afarensis* have been recovered from fluviolacustrine sediments at Hadar through 2012. The species is also definitively represented in similar-age deposits of several other Afar basin sites (including Dikika, Ledi-Geraru, Woranzo-Mille, and Maka) and in the Koobi Fora Formation, at Koobi Fora, Kenya. The oldest known fossils of the species, including the type specimen (a mandible, LH-4), occur in the Upper Laetolil Beds (3.5–3.8 Ma), at Laetoli, northern Tanzania.

Lucy and other specimens of *A. afarensis* epitomize the mosaic emergence of human anatomy during the early evolution of our lineage (Kimbel and Delezene 2009). The cranium and jaws retain many features from the common ancestor we shared with chimpanzees, including a small brain (350–550 cc) and projecting snout, but the relatively low-crowned canine teeth wore down from their tips as in modern humans. While *Lucy*'s hip, knee, and foot were adapted to a balanced two-legged stride, with fully extended knee and powerful push-off at the great toe, she had long, powerful arms and curved fingers, reminiscent of the tree-climbing anatomy of the great apes. These anatomical contrasts have been fodder for intense scholarly debate regarding the adaptations of our early ancestors (Ward 2002).

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Paleosol

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Paleosol is defined as a soil that formed on a landscape of the past (Yaalon et al. 1971; Retallack 2001). The definition of paleosol is not straightforward as it can vary by geologic discipline. Quaternary geologists often define paleosols as having been buried, exhumed, and/or at the surface as relict soils. In this case, a paleosol must contain evidence of a nonextant soil-forming environment, e.g., glacial climate (Birkeland 1999). Geologists who primarily work in the pre-Quaternary often define paleosols as lithified, fossil soils that document a past landscape (Retallack 2001).

Like modern soils, paleosols record evidence of the physical, chemical, or biological alteration of a preexisting material to a more stable form, i.e., weathering. These weathering features formed partly as a result of five primary environmental factors: (i) climate, (ii) organisms, (iii) relief, and (iv) parent material operating through (v) time (Jenny 1941). Paleosols are therefore valued for their record of paleoenvironment(s) and paleoclimate(s) in both Quaternary and pre-Quaternary records. Because paleosols record past landscape conditions through an interval of time, they are often subject to a variety of dating methods. Generally speaking, dating methods applied to soils and paleosols are used to assess the duration of soil formation and/or provide a numerical age estimate during which the soil formed.

The duration of formation may be assessed qualitatively, e.g., “young” or “old” soil, or quantitatively, e.g., a soil formed for 2,000 years. Soil geomorphologists study how modern soils vary as a function of time when all other properties are held constant, i.e., a soil chronosequence (Jenny 1941; Birkeland 1999; Holliday 2004 – see Table 7.2). A number of profile properties have been shown to vary as a function of duration of soil formation, young to old. Age-related properties derived from chronosequences have been used in geomorphic and geoarchaeological research of paleosols; however, there are a number of potential pitfalls and caution should be exercised when trying to obtain a numerical age estimate using this approach (Holliday 2004).

Absolute dating methods are applied to paleosols and buried soils to derive numerical estimates. Common approaches include radiocarbon (^{14}C), U-series, luminescence techniques, and cosmogenic-nuclide exposure dating (Holliday 2004; Balco and Rovey 2008). Radiocarbon is perhaps the most frequently method used to derive a numerical age estimate for late Quaternary paleosols (Holliday 2004). Radiocarbon of soil organic matter from a buried surface horizon can be dated to derive an apparent mean residence time (Holliday 2004 and references therein). Both radiocarbon and luminescence dating have been applied to eolian and alluvial parent materials on which the paleosol formed to derive a maximum numerical estimate (age-maxima) of soil formation (Holliday 2004).

U-series dating has been applied to pedogenic carbonates to assess the age of a paleosol or buried soil (Holliday 2004). Recent advances in cosmogenic-nuclide exposure dating have refined the burial-age estimates for paleosols using an isochron approach (Balco and Rovey 2008). The slope

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of ^{10}Be and ^{26}Al from concentration profiles in paleosols has been used to derive a numerical estimate of burial age.

Cross-References

- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Luminescence Dating](#)
- ▶ [14C Dating](#)
- ▶ [U-Series Dating](#)

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Thermochronology, Detrital Zircon

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Definition

Detrital zircon thermochronology is the study of thermal histories of rocks revealed through cooling ages obtained from detrital zircon. Most studies focus on fission-track or helium dating of suites of single grains to reveal the thermal evolution of a source region.

Introduction

Detrital zircon thermochronology is focused on the evaluation of ages of detrital zircon grains to reconstruct the thermal evolution of source rocks that supplied sediment to a basin. Zircon (ZrSiO_4) is an accessory mineral that crystallizes primarily in silica-rich igneous rocks, but after erosion and deposition it occurs widely in sedimentary rocks and their metamorphic equivalents (Bernet and Garver 2005). Because zircon is very durable in typical sedimentary environments on Earth, it typically survives sedimentary transport and in fact can be concentrated in heavy mineral assemblages where mineralogical fractionation occurs naturally by sedimentary processes. Zircon is also resistant to chemical attack and thus can also survive interaction with basin fluids that may affect host strata during burial and diagenesis. Because of this durability, zircon can be polycyclic and survive multiple sedimentary cycles (Poldervaart 1955).

Zircons contain trace amounts of non-formula elements of which uranium and thorium are most important because these elements decay through natural radioactive disintegration (Hancher and Hoskin 2003). A typical detrital zircon will contain between 100 and 1,000 ppm uranium, and the U:Th ratio is generally between about 2:1 to 1:1 (Garver and Kamp 2002), although metamorphic zircons are known to have very high thorium concentrations (Rubatto 2002). Because of the relative abundance of uranium and the difference in decay rates, uranium is of primary importance in detrital zircon studies.

Radioactive Decay in Zircon

Uranium decays through two modes. The primary mechanism of decay is α -decay in which uranium decays to lead (Pb) through a series of intermediate daughter elements and the ejection of α -particles (^4He) (Reiners 2005). During the decay of ^{238}U , the most common isotope of uranium, radioactivity in this decay chain results in the release of eight α -particles (see ► [U-Th:He Dating](#)). Uranium can also disintegrate through spontaneous fission, but this process is much less common (by a factor of about 2×10^6) (Tagami 2005). Spontaneous fission results in two subequal energetic fragments of the original uranium atom that recoil away from one another through the crystal lattice, and in the process, they produce an amorphous zone of disorder that is <10 nm wide and about 10,000 nm long

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(10 μm) (Wagner and van den Haute 1992). This zone of disorder is called a fission track (see ► [Fission-Track Dating and Thermochronology](#)). Single detrital zircon grains are routinely dated using helium dating or fission-track dating to understand the thermal evolution of the source rocks. Most published studies of zircon thermochronology use the fission-track method (see Garver et al. 1999; Bernet and Garver 2005; Reiners and Brandon 2006).

Closure Temperatures

Effective closure of the isotopic system is a key aspect of analysis in detrital thermochronology (Reiners and Brandon 2006). For zircon helium dating (ZHe), closure occurs at about 180 °C, and in zircon fission-track (ZFT) dating, effective closure occurs in a window between about 250 °C and 340 °C (see discussion Reiners and Brandon 2006; Tagami 2005; Bernet 2009). In both cases, closure or annealing appears to be partly governed by total radiation damage and rate of cooling. Thus, in detrital thermochronology, zircons provide information about the low-temperature cooling history (180–340 °C) of the source region (Garver et al. 2005). Note that this is fundamentally different from information provided by U/Pb dating of single zircon grains (see ► [Uranium-Lead, Detrital Zircon](#)), because the former technique provides information on the cooling history of the source terrane and the latter provides the crystallization age. Because zircon can be polycyclic, some detrital zircon U/Pb ages may provide age information on what was ultimately the original source rock, but these rocks may be unrelated to the orogenic cycle that produced a sediment source (see discussion in Bernet and Garver 2005). With ZHe or ZFT dating, the thermal signature of the sediment-source terrane is evaluated. In most cases, this is directly related to orogenesis and tectonic processes related to uplift and exhumation in orogenic belts (Garver et al. 1999). Thus, detrital thermochronology is the preferred approach if the goal is to understand the direct relationship between source terrain evolution and basin sedimentation (as in Fig. 1; see Garver et al. 1999; Carter and Bristow 2000).

Exhumation and Erosion

Detrital zircon grains provide a rich record of the cooling history of source terrains that eroded to supply sediment to adjacent sedimentary basins (Fig. 1; see Bernet et al. 2004). Rocks in a source terrain are exhumed by tectonic or erosional processes, meaning that they are brought from lower levels in the crust to the surface. The process of exhumation allows for rocks to move upward in the crustal column to the surface. In this setting, rocks pass through the closure temperature (T_c) for a particular dating system as they transit to the surface. Exhumation rates of the orogenic belt can be determined provided a number of key variables can be reasonably constrained: these include the closure temperature (T_c), the geothermal gradient, and time required to erode and transport detritus to an adjacent sedimentary basin (in Fig. 1, $t_c - t_d$). Together, the transit time past the closure isotherm and the time required to transfer detritus to a sedimentary basin are referred to as the *lag time* (in Fig 1, this is $t_c - t_d$; see Brandon and Vance 1992; Garver and Brandon 1994; Garver et al. 1999). In virtually all orogenic settings, there is a lag between closure and deposition, which is primarily a function of exhumation rates (Garver et al. 1999; Bernet and Garver 2005; Reiners and Brandon 2006). Thus, detrital zircon thermochronology has been extensively used to better understand exhumation rates of rocks in orogenic belts (for examples, see Brandon and Vance 1992; Bernet et al. 2004; Spiegel et al. 2004; Ruiz et al. 2004; Enkelmann et al. 2009; Whitchurch et al. 2011).

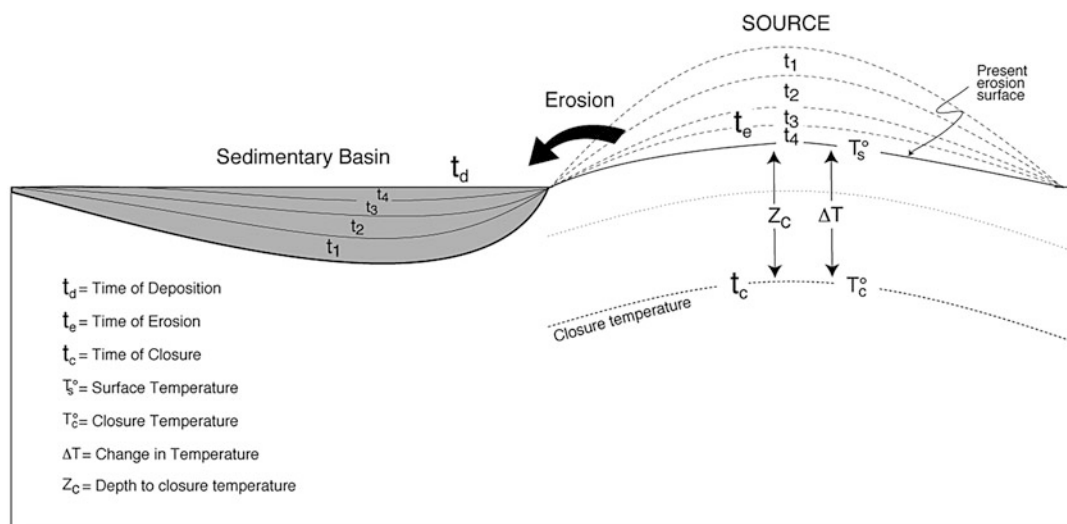


Fig. 1 Schematic diagram showing the relationship between exhumation and erosion in the source region and deposition of eroded material in a flanking basin. In detrital thermochronology, zircons eroded from the source terrain are deposited in sequential layers in a basin. Zircons in rocks are exhumed from depth and in the process pass through an effective closure isotherm during transit to the surface. To relate closure temperature to depth of exhumation, some assumptions need to be made about the temperature of closure and the geothermal gradient (Modified from Garver et al. 1999)

Zircon Thermochronology Studies

Many traditional studies have focused on Mesozoic and early Cenozoic basin settings (Brandon and Vance 1992; Bernet et al. 2001; Ruiz et al. 2004; Spiegel et al. 2004; Whitchurch et al. 2011). A number of recent studies have used modern detritus from active orogenic belts to understand exhumation, and many of these have been focused on fast-exhuming orogenic belts where sedimentary storage between erosion and deposition is negligible. In very-fast-exhuming mountains, the cooling ages can be less than 5 Myr and in some cases less than 1 Myr. Detrital grains that are this young provide a few analytical challenges because the small number of daughter products (helium or a fission track) generated during this period can be difficult to detect. An additional challenge in these settings is the significant advection of the isotherms in the source terrain and the requirement for modeling how isotherms may have changed during orogenic evolution (Reiners and Brandon 2006). In the Chugach-St. Elias orogen (Alaska), ZFT cooling ages from modern rivers and glaciers indicate a local area of intense erosional exhumation where grain ages are less than 3 Ma. This result illuminates the relationship between surface processes (glacial erosion) and tectonics processes at the junction of a tectonic boundary (Enkelmann et al. 2009).

While there is no theoretical limit to how old a zircon can be to provide useful thermochronological information, there are some practical and analytical considerations that make analysis of exhumation rates of Precambrian terrains difficult. Part of the analytical challenge is that the high density of fission tracks and the amount of radiation damage in ancient grains can hinder analysis and systematic behavior of zircons (Montario and Garver 2009). To study Precambrian thermochronology, it is important to understand the thermal history of the strata because many sedimentary sequences have been heated to temperatures sufficient to anneal fission tracks or to allow the loss of helium ($>180\text{--}200\text{ }^{\circ}\text{C}$). Detrital zircon in Cambrian strata that sit uncomfortably above the Grenville basement rocks (Mesoproterozoic, c. 1,000–1,250 Ma) in New York State (USA) were dated using high-resolution ZFT dating using a scanning electron microscope (SEM) to

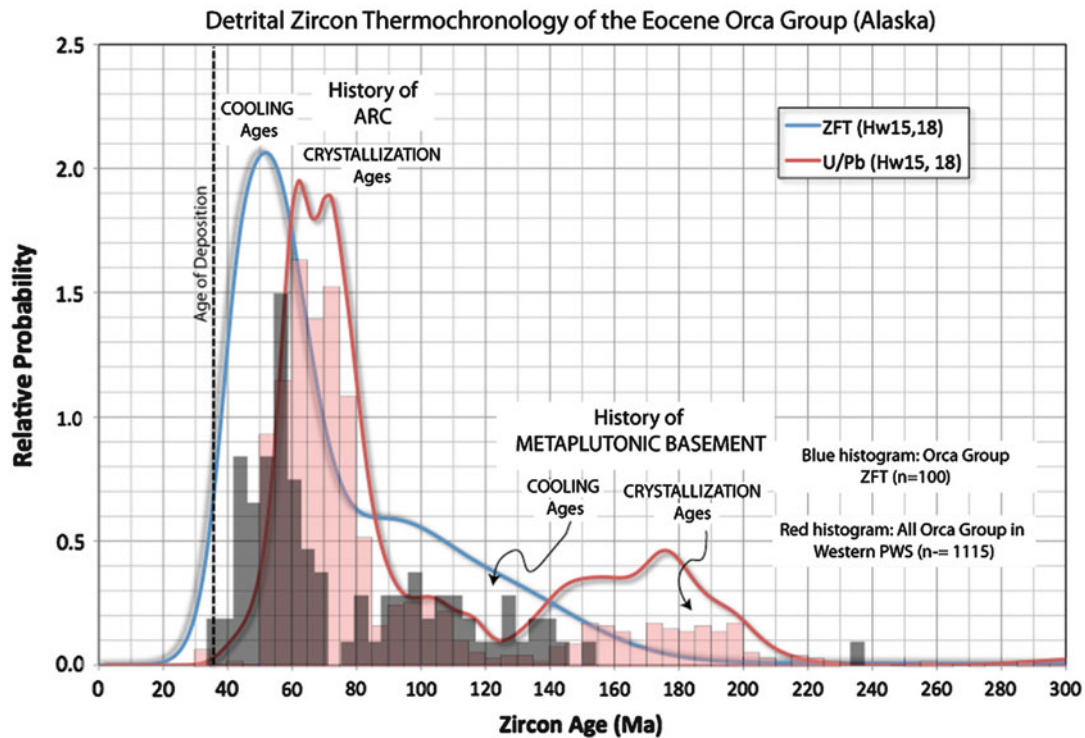


Fig. 2 Example of a detrital zircon study from Eocene strata of the Orca Group in southern Alaska (Modified from Carlson 2012). In this study, 100 detrital zircons were dated using zircon fission track, and then the crystallization age of each grain was determined by LA-ICP-MS. This double dating allows for a detailed understanding of how arc volcanics and the metaplutonic basement have clear and distinct thermal histories that are recorded in detrital zircon grains

image and count fission tracks (Montario and Garver 2009). In the case of the exhumation of the Grenville basement, post-Grenville exhumation was recorded at ~780 Ma, followed by basement heating related to the rifting of Rodinia at ~540 Ma – both events occurring during the Neoproterozoic (Montario and Garver 2009). In this study, apparent single-grain cooling ages as old 2.0 Ga were obtained.

In many detrital zircon thermochronologic studies along convergent margins, there can be a significant number of quickly cooled zircon grains that represent near-surface volcanic or plutonic activity. In these cases, the cooling age may represent volcanic activity and may be unrelated to exhumation of rocks in a source terrain (Garver et al. 2000). It can be difficult to determine if a single-grain age is the result of a volcanic eruption that cooled at the surface or the result of intrusion followed by rapid exhumation from greater depth. One approach used to address this situation is to double-date single grains using both low-temperature methods (i.e., fission track) and U/Pb methods (i.e., high temperature; see Fig. 2). Those grains with concordant low- and high-temperature ages are inferred to have a volcanic origin.

Analytical methods have improved in recent years, and dating of single crystals by two or more methods is possible, but not yet routine. Because FT dating of zircon is not destructive, a zircon can be dated after ZFT by either LA-ICP-MS or ZHe approaches (both of which are destructive). This approach allows for an incredibly informative data set where single crystals reveal details about when rocks were formed and when they were cooled (Carter and Bristow 2000; Rahl et al. 2003; Reiners et al. 2005; Carlson 2012). An example from the Eocene Orca Group in the accretionary complex of southern Alaska (Fig. 2) shows ZFT and U/Pb double dating that reveals the relatively simple thermal evolution of the volcanic arc complex in the Cretaceous and the more protracted

formation of a lower Mesozoic basement complex that was exhumed in the Early Cretaceous. This data set contains some detrital zircons that are volcanic (rapidly cooled) because the ZFT and U/Pb ages are concordant within error (see Carlson [2012](#)).

For detrital zircon in basin strata to retain provenance information, the host strata must have remained below the annealing temperature for its entire history; otherwise, the zircon may have its thermal record reset or partially reset (Bernet and Garver [2005](#)). For the FT system, this means that basin strata must remain below temperatures of about 200 °C; otherwise, resetting or partial resetting can compromise provenance information. Nevertheless, data from those settings may be useful to better understand postdepositional heating of the basin (Garver et al. [2005](#)).

Summary

Detrital zircon thermochronology is the study of the thermal histories of source terrains that shed sediment into flanking basins. The primary aim of most studies is to use cooling ages in sedimentary detritus to reconstruct the temporal framework of exhumation in orogenic highlands that supply sediments to basins. Most published studies use fission-track dating on single zircon grains, but there is an emerging literature where helium dating is used (Reiners and Brandon [2006](#)). Cooling ages of single zircon grains can be related to exhumation of crustal rocks in an orogenic belt or high-level volcanic activity. In young rapidly exhumed orogenic belts, populations of cooling ages may be 1 Myr or less than crystallization ages. In old terrains, Precambrian cooling ages have been determined and used to understand source evolution. If basin strata have been heated to temperatures of 180–200 °C, the original thermal record of the source rock may be compromised (annealed or partly annealed); however, the reset grains may then provide information about postdepositional thermal events.

Cross-References

- ▶ [Exhumation \(Thermochronology\)](#)
- ▶ [Fission Track Dating](#)
- ▶ [⁴He/³He Dating](#)
- ▶ [Provenance \(Thermochronology\)](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Erosion \(Thermochronology\)](#)
- ▶ [Uranium-Lead, Detrital Zircon](#)
- ▶ [Uranium-Lead, Zircon](#)
- ▶ [U-Th:He Dating](#)
- ▶ [Zircon](#)

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Thermochronology, Meteorites

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Definition

A field of research constraining thermal histories of meteorites (rocks produced in extraterrestrial environment and delivered to Earth) and interpreting the results in the context of Earth and planetary science.

Introduction

Since the formation of our solar system at 4,568.2 Ma (Bouvier and Wadhwa 2010), individual solid objects in the solar system experienced a range of planetary processes associated with temperature changes. Accretion, impact, breakup, metamorphism, and alteration are some of these planetary processes, which provide valuable information into the early evolution of the solar system. In addition, peak temperature conditions and cooling paths are crucial in understanding various physical properties (e.g., dimensions, internal structures) of solid bodies. The field of research known as “thermochronology” provides a means of investigating the thermal histories of meteorites (or their parental rock bodies) and interpreting the resulting data.

Methods

Thermal histories of meteorites can be constrained from multiple independent approaches. Peak temperature conditions of meteorites, particularly during thermal metamorphism or shock events, are commonly estimated based on phase equilibria, microscopic textures, refractive indices, and natural remanent magnetization data. Cooling rates of meteorites are constrained using metallographic textures, elemental diffusion in minerals, and ^{244}Pu fission tracks. Absolute ages and corresponding temperature conditions are investigated through radioisotopic thermochronometers. Radioactive decay is a natural process where an unstable parent isotope releases energy as it transforms to one or more daughter isotopes (“► [Radiation and Radioactivity](#)”). Because the rate of decay for a given radioactive isotope is nearly constant regardless of the physical conditions or types of hosting materials, the age can be determined by measuring the abundances of parent and daughter isotopes. Each element has unique diffusion properties in the host materials, allowing ages determined for various geochronological systems to be associated with a range of temperature conditions experienced by the host material. Therefore, a time-temperature path can be deduced by studying one or more radioisotopic systems. U-Th-Pb (“► [Uranium-Lead, Extraterrestrial, Early Solar System](#)”; Bouvier et al. 2007), $^{40}\text{Ar}/^{39}\text{Ar}$ (“► [Extraterrestrial Materials \(K-Ar/Ar-Ar\)](#)”; Turner et al. 1978; Bogard 2011), and (U-Th)/He (“► [U-Th:He Dating](#)”; Min 2005) thermochronometers are most commonly used for meteorites.

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Case Studies

H Ordinary Chondrites

H chondrites comprise the most distinctive group among officially identified meteorites. They are by far more abundant than other types of ordinary chondrites and provide one of the most complete descriptions of their parent asteroid. Thermal histories of H chondrites were extensively investigated using nearly all the available thermochronologic methods in order to understand accretion process, metamorphism, internal structure, physical dimension, and shock impact history of the parent body.

After the accretion of the H parent body, it experienced thermal metamorphism during its early history primarily due to the radioactive decay of ^{26}Al . Early investigations of U/Pb systematics revealed that many H5–H6 chondrites cooled through the closure temperatures of phosphates during the first ~60 Myr after formation of Ca–Al-rich inclusions (CAIs) (Göpel et al. 1994). Based on U/Pb systematics of the Richardton meteorite (type H5 ordinary chondrite), it was suggested that the accretion of the H parent body was initiated at 1.7 Ma after the formation of CAIs and continued for 3.5 Ma (Amelin et al. 2005). Similar conclusions were derived using Hf/W systematics, which suggested that the accretion was started no earlier than ~1.7 Ma after the formation of CAI, was almost completed by ~6 Ma, and was followed by peak metamorphism until ~10 Ma (Kleine et al. 2008).

A layered internal structure was suggested for the H parent body. This “onion shell model” posits that H meteorites are derived from different depths in a hypothetical parent body where the highly metamorphosed meteorites (H6) from the inner part of the parent body were surrounded by successive shells of lower-grade rock (H5–H3) (Wood 1967; Hutchison et al. 1980; Pellas and Storzer 1981). This model predicted an inverse correlation between peak metamorphic temperatures and cooling rates. However, cooling rates determined from the metallographic methods were not consistent with the suggested inverse correlations. Consequently, the “metamorphosed-planetesimal model” was proposed (Scott and Rajan 1981), which proposed that the maximum metamorphism occurred in small planetesimals, followed by accretion that formed the chondritic parent body. A slightly revised model was suggested: collision-driven fragmentation of an onion shell body during the peak metamorphism followed by a rapid reassembly (Grimm 1985; Taylor et al. 1987). Subsequent thermochronologic studies on Hf/W (Kleine et al. 2008), U/Pb (Göpel et al. 1994; Blinova et al. 2007), $^{40}\text{Ar}/^{39}\text{Ar}$, and ^{244}Pu fission tracks (Trieloff et al. 2003) revealed the inverse relationship for a large number of H chondrites for both high- and low-temperature regimes, supporting the onion shell model (Harrison and Grimm 2010). Simulations of the thermal histories based on the onion shell model (Miyamoto et al. 1981; McSween et al. 2002) imply a relatively small parent body (radius = ~50–100 km). However, thermal histories of some H chondrites cannot be explained by a simple monotonic cooling predicted by the onion shell model (Kessel et al. 2007). Data for those rocks require modifications of the simple model that include fragmentation and reassembly of the onion shell parent body (Ganguly et al. 2013).

Shock impact is one of the major planetary processes which generate a significant amount of heat, thus resetting many isotopic chronometers, particularly K/Ar and (U–Th)/He. Three major impact periods were identified for H chondrites primarily through $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometer: at >4.45 Ga (planetary accretion phase), at 4.1–3.5 Ga (lunar cataclysm), and at <1 Ga (Bogard 1995; Swindle et al. 2009, 2013).

L and LL Ordinary Chondrites

Cooling histories of LL chondrites were investigated using I/Xe (Bernatowicz et al. 1988), U/Pb (Göpel et al. 1994; Bouvier et al. 2007), $^{40}\text{Ar}/^{39}\text{Ar}$ (Hohenberg et al. 1981), (U–Th)/He (Min

et al. 2013), and ^{244}Pu fission tracks (Pellas and Storzer 1977, 1981). Their post-metamorphic cooling rate is generally lower than H chondrites, suggesting that the LL asteroid had a larger dimension than the H parent body (Pellas and Storzer 1981; McSween et al. 2002; Bouvier et al. 2007).

L chondrites with clear evidence of shock are more common than H and LL chondrites. $^{40}\text{Ar}/^{39}\text{Ar}$ and (U-Th)/He ages of L chondrites are significantly younger than H and LL chondrites, most likely caused by impact-related heating in their parent body (Heymann 1967; Bogard et al. 1976, 1995; McConville et al. 1988; Wasson and Wang 1991; Korochantseva et al. 2007). The ages are highly clustered in a range of ~400–500 Ma, which is commonly suggested as the timing of catastrophic breakup of their parent body. A large number of fragments of L chondrites were discovered within mid-Ordovician (~470 Ma) sedimentary layers, thereby supporting the hypothesis that the parent body of L chondrites was rapidly delivered to Earth after the catastrophic disruption of the parent asteroid (Schmitz et al. 2001, 2003; Heck et al. 2004, 2008).

Acapulco Meteorite

Based on petrographic observations (McCoy et al. 1996), Ca zoning patterns in olivine (Zipfel et al. 1995), and Fe-Mg ordering in orthopyroxene (Zema et al. 1996), the primitive achondrite Acapulco is thought to have cooled rapidly from ~1,100 °C to ~350 °C. These constraints, combined with absolute ages from Hf/W (Touboul et al. 2009) and $^{207}\text{Pb}/^{206}\text{Pb}$ systematics (Göpel and Manhès 2010), suggest a more detailed thermal history with a cooling rate that peaked at ~4,556 Ma, which was interpreted to be the timing of a breakup of the parent body. The cooling path below ~350 °C is controversial. $^{40}\text{Ar}/^{39}\text{Ar}$ and ^{244}Pu fission track data suggest a significant reduction of cooling rate below ~350 °C (Pellas et al. 1997), which can be related to the reassembly of the broken pieces immediately after the breakup. However, the suggested cooling rate change at ~350 °C was questioned based on the revised decay constant of ^{40}K (Kwon et al. 2002) combined with new $^{40}\text{Ar}/^{39}\text{Ar}$ data (Renne 2000). (U-Th)/He ages obtained from single phosphate grains are identical to the age of the solar system within their uncertainties and are significantly older than expected from ^{244}Pu fission track data, suggesting the possibility of a rapid cooling down to ~100 °C (Min et al. 2003).

ALH84001 Martian Meteorite

ALH84001 is one of the most important Martian meteorites because of its exceptionally old crystallization ages (Sm/Nd age = 4.41–4.57 Ga, Rb/Sr age = 3.84–4.55 Ga) and its long residence in the Martian crust. $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ~3.8–4.2 Ga are commonly attributed to an intense period of impacting of the Martian surface (Ash et al. 1996; Turner et al. 1997; Bogard and Garrison 1999). A number of young and scattered (U-Th)/He ages on phosphate grains (0.1–1.5 Ga; Min and Reiners 2007) and whole-rock Ar diffusion kinetics (Cassata et al. 2010) suggest the existence of one or more high-temperature shock events after the primary impact at ~4.0 Ga. Based on the Ar diffusion modeling, the temperature of the Martian surface was estimated to be cold (<~22 °C) for most of the past ~4.0 Ga (Shuster and Weiss 2005; Cassata et al. 2010).

Summary and Conclusions

To investigate thermal histories of meteorites, a wide range of thermochronologic tools are used. Some constrain cooling rates or relative temperature changes over age differences, whereas others yield absolute timings of when the meteorites cooled down to certain temperatures. The current

understanding of the thermal histories of meteorites provides crucial information of various planetary processes, internal structures and physical dimensions of the parent bodies, as well as the surface temperature evolution of the Martian crust.

Cross-References

- ▶ [Extraterrestrial Materials \(K-Ar/Ar-Ar\)](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Uranium-Lead, Extraterrestrial, Early Solar System](#)
- ▶ [U-Th/He Dating](#)

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Environmental Releases

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Definition

Environmental Forensics. The systematic and scientific evaluation of physical, chemical, and historical information for the purpose of developing defensible scientific and legal conclusions regarding the source or age of a contaminant release into the environment (Morrison and Murphy 2013).

Introduction

The study of contaminant releases into the environment is termed *environmental forensics*. Forensic techniques used to date and identify the origin of a contaminant release include dendroecology, aerial photogrammetry, compound-specific isotopic analysis (CSIA), congener analysis, contaminant transport modeling (liquid and colloidal), molar ratio analysis, biological, isotopic, and chemical pattern recognition, corrosion modeling, lipid and associated biological techniques, scanning electron microscopy (SEM), and advanced multicomponent analysis of chemical data. The following text describes selected techniques used to identify the source and age of a contaminant release into the environment.

Source Identification

Forensic techniques for identifying a contaminant source are often similar to environmental investigations designed to define the areal extent of a contaminant release for remediation purposes. Environmental forensics transcends traditional investigative techniques, however, by employing scientific techniques in combination to identify and discriminate between sources of a contaminant release. Three approaches used to identify contaminant sources include (1) association of a diagnostic chemical with a particular use and/or time frame; (2) chemical, biological, and isotopic techniques; and (3) congener analysis.

Diagnostic Chemicals Used for Source Identification

Examples of diagnostic chemicals indicative of a discrete production time frame for source identification and release dating in the United States (USA) include (USEPA 1978; Kaplan et al. 1997; ATSDR, 2002a, b; Morrison and Murphy 2006):

- 1,4-dioxane with methyl chloroform indicative of a post-1951 release
- Monsanto Aroclor 1016 (produced between 1971 and 1974)
- Aroclor 1260 as the predominant Aroclor used in electrical transformers prior to 1971

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- Cessation of DDT production in 1972, aldrin/dieldrin in 1974, and mirex in 1962 to 1978
- The gasoline oxygenate methyl tertiary butyl ether (MTBE) as indicative of a post early-1980s release

Diagnostic chemicals in a formulation specific to a particular application offer the potential to link a chemical with a particular temporal activity; an example is the presence of the stabilizer thymol with trichloroethylene (TCE) as indicative of pharmaceutical grade TCE used prior to 1984 (Totonidis 2005). The presence of octene, nonene, and *n*-pyrrole with tetrachloroethylene (PCE) in an environmental sample is indicative of its use as a dielectric fluid in electrical transformers, likely in the 1980s (Morrison and Murphy 2013). A substantial body of peer-reviewed literature is available that describes using diagnostic chemicals for source identification and/or dating of contaminant releases (Morrison 1999, 2013; Murphy and Morrison 2002, 2007, 2014; Morrison and Murphy 2006; Peters et al. 2007; Morrison and O'Sullivan 2010, 2012, 2014).

Chemical, Biological, and Isotopic Techniques

Chemical techniques for source identification include molar ratio analysis and degradation relationships, including the chlorinated solvent PCE degradation series ($\text{PCE} \rightarrow \text{TCE} \rightarrow 1,2\text{-DCE} \rightarrow \text{vinyl chloride}$) for which common plots include $[\text{TCE}/\text{PCE}]$, $[\text{DCE}/\text{TCE}]$, $[\text{DCE}]/[\text{PCE} + \text{TCE}]$, $[\text{cis} + \text{trans } 1,2 \text{ DCE} + \text{VC}]/[\text{PCE} + \text{TCE}]$, $[\text{VC}]/[\text{PCE} + \text{TCE}]$, $[\text{cis} + \text{trans- } 1,2\text{DCE}]/[\text{PCE} + \text{TCE}]$, and $[\text{VC}]/[\text{cis} + \text{trans-}1,2 \text{ DCE}]$ as a means to identify and discriminate between multiple sources of PCE. Techniques used to distinguish sources for crude petroleum hydrocarbons include diagnostic biomarker ratios, including acyclic isoprenoids (e.g., (pristine)/(phytane), (pristine)/(*n*-C₁₇) and (phytane)/(*n*-C₁₈), terpanes (e.g., (C₂₁)/(C₂₃ tricyclic terpane) and (C₂₈bisnorhopane)/(C₃₀αβ hopane)) and steranes (e.g., (C₂₇αββ/C₂₉αββ steranes at *m/z* 218) and (C₂₈αββ)/(C₂₇αββ + C₂₈αββ + C₂₉αββ) at *m/z* 218) (Morrison and Murphy 2006). The normalized distribution, ratios and cross-plots of polyaromatic hydrocarbon (PAHs) sources are similarly available for source identification (Fig. 1), some of which are used to distinguish between petrogenic and anthropogenic sources (e.g., (fluoranthene + pyrene)/(C₂+C₃+C₄ phenanthrenes) and (phenanthrene/anthracene) versus (fluoranthene/pyrene)) (Fig. 2) (Morrison and Murphy 2006; Wang and Stout 2007; Wenning and Martello 2014).

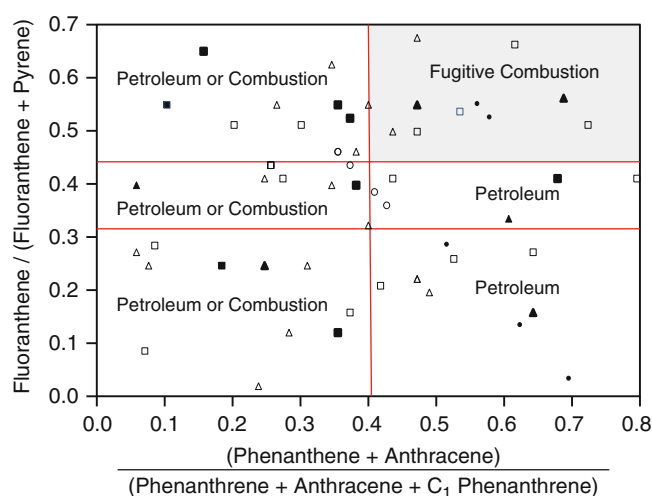


Fig. 1 Normalized cross-plots of polyaromatic hydrocarbons used to distinguish between petrogenic and anthropogenic sources of petroleum hydrocarbon releases

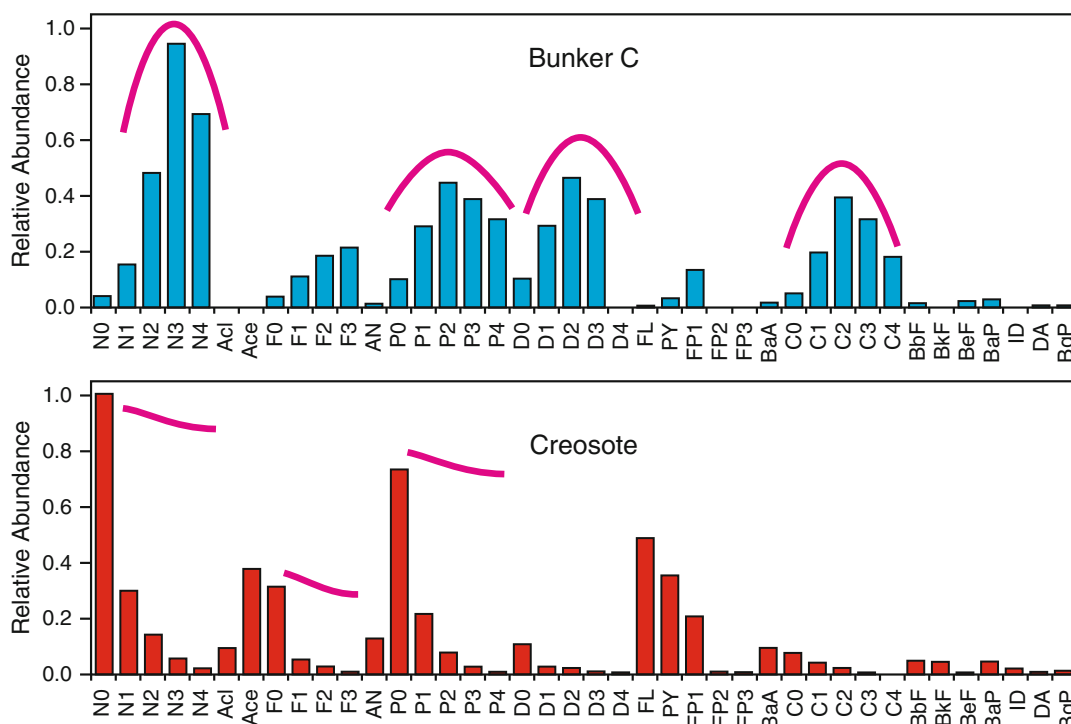


Fig. 2 Normalized histogram using the relative abundance of various polycyclic aromatic hydrocarbons (PAHs) listed along the x-axis to distinguish between creosote and Bunker C fuel

For distinguishing a release from a sanitary sewer from other sources, detergent metabolites including 4-*n*-octylphenol, 4-*tert*-octylphenol, diethoxynonylphenol, NPEO-2, OPEO-2, ethoxynonylphenol NPOE-1, ethoxyoctylphenol OPEO-1, and 4-nonylphenol are available. Other indicators include pharmaceutical indicators, trihalomethanes, and human fecal bacteria such as *Bacteroidales* and viruses (i.e., hepatitis A, adenovirus, and enterovirus). Other biological markers include sterols (i.e., cholesterol, β -sitosterol, 3 β -coprostanol, and stigmastanol, β - and α -cholestanone, campesterol, stigmastanol, and epicoprostanol) as indicators of fecal contamination. The fecal sterol 3 β -coprostanol is produced in the gut of some mammals, including humans, pigs and cats, by the microbially mediated reduction of cholesterol under anaerobic conditions. Sterols and stanols can be combined to distinguish between the release of feces containing swine and cow waste. The specificity of steroids as a means to differentiate cow feces from pig slurries is available by considering fecal stanol diagnostic compounds, including coprostanol, epicoprostanol, campenstanol, sitostanol, 24-ethylcoprostanol and 24-ethylepicoprostanol and/or their ratios. Another forensic opportunity is the detection of nanoparticles (1–100 nm), such as nanosilver (*n*-Ag) and nano-titanium oxide (*n*-TiO₂) that are associated with fabric and exterior paints, respectively, in environmental samples as surrogates for the releases of contaminants from these potential sources (Benn and Westerhoff 2008).

Bulk and compound-specific isotopic analysis (CSIA) can be used to identify and discriminate between different sources of contamination. Examples of the use of CSIA and bulk isotope analysis include whether methane gas is biogenic or anthropogenic (¹H/²H); the origin of sulfur from naturally occurring hydrothermal sulfate or from the oxidation of reduced sulfur in pyrite-rich ore materials using four stable isotopes (³²S, ³³S, ³⁴S, ³⁶S); discrimination between sources of crude oil releases (¹³C/¹²C); characterization of the biochemical evolution of dissolved organic carbon; examination of biodegradation of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) using δ^{15} N and

$\delta^{18}\text{O}$ enrichment; MTBE (methyl tertiary butyl ether) source identification using ($^{13}\text{C}/^{12}\text{C}$); the origin (naturally occurring or anthropogenic) of perchlorate using $^{18}\text{O}/^{16}\text{O}$, $^{35}\text{Cl}/^{37}\text{Cl}$, and $^{17}\text{O}/^{16}\text{O}$ ratios; the kinetics of natural attenuation/degradation of contaminants; the origin of PCBs, pesticides, and lead; the identification of sulfur sources using stable sulfur isotope signatures; and the origin of PCE and TCE using differences in carbon, chlorine, and/or hydrogen isotope ratios. In hydrology investigations, isotopes are used to estimate ages of groundwater based on $^{18}\text{O}/^{16}\text{O}$ and assumptions about past temperatures and recharge compositions. In environmental forensic investigations, the primary isotopes and ratios include hydrogen ($^2\text{H}/^1\text{H}$), carbon ($^{13}\text{C}/^{12}\text{C}$), nitrogen ($^{15}\text{N}/^{14}\text{N}$), oxygen ($^{18}\text{O}/^{16}\text{O}$), sulfur ($^{34}\text{S}/^{32}\text{S}$), and for chlorinated solvents, chlorine ($^{37}\text{Cl}/^{35}\text{Cl}$).

CSIA is also used to distinguish between naturally occurring and anthropogenic sources of chloroform in soil gas and groundwater. In one study, $\delta^{13}\text{C}$ values of chloroform (-22.8 to -26.2 ‰) in soil gas collected in a forested area were within the same range as values from the soil organic matter (-22.6 to -28.2 ‰) but were more enriched in ^{13}C compared to industrial chloroform ($\delta^{13}\text{C}$ values of -43.2 to -63.6 ‰ (Hunkeler et al., 2012)).

Congener Analysis

The term congener refers to individual compounds, regardless of their homologue class. PCBs, dioxins, and furans are conducive to congener analysis for source discrimination. Figure 3 is a normalized histogram for virgin PCE solvent and sludge residue from a distillation still at a facility in Japan (Fukai and Nakata 2001). Many of the chlorinated dibenzodioxins (CDDs) and chlorinated dibenzofurans (CDFs) in the new PCE solvent in Fig. 3 are OCDD and HpCDD enriched in the distillation sludge, thereby providing a potential means to (a) develop a working hypothesis regarding the source of the PCE and CDD/CDF compounds found with a particular PCE/dioxin/furan profile and (b) whether the PCE originated from new or spent PCE.

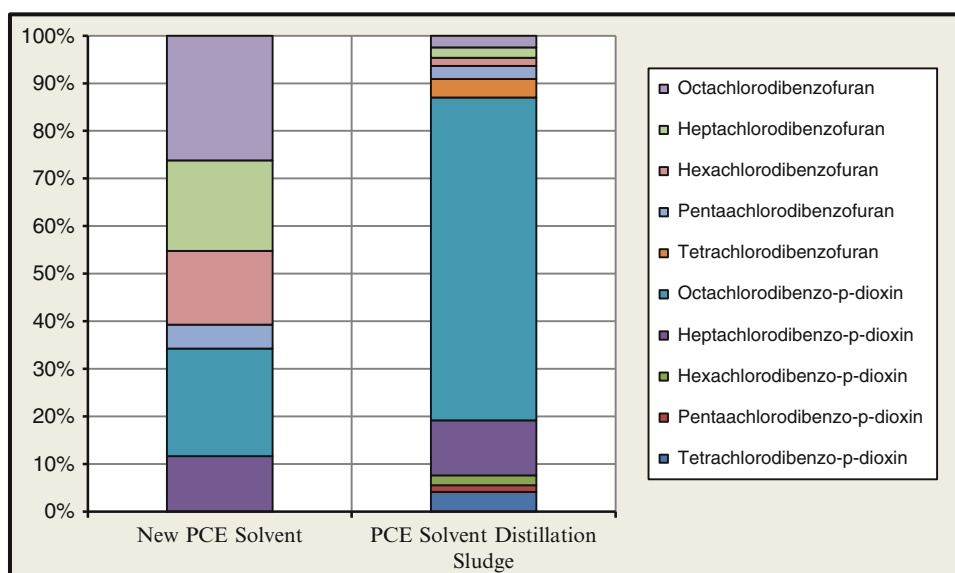


Fig. 3 Normalized histogram of TCDD and PCDD congeners in new PCE solvent and in distillation sludge from a dry cleaning facility using PCE

Dating a Contaminant Release

Forensic techniques used for source identification can often bracket the time when a release occurred. Another approach is contaminant transport modeling of atmospheric, surface, and sub-surface releases of contaminants. Forensic contaminant transport models include simulations to identify the age of contaminant releases in the atmosphere, liquid releases on a paved/unpaved surface, liquid transport through the unsaturated zone, vapor transport, and intrusion models in soil and groundwater models. Groundwater models used to date a contaminant release include (a) measuring the leading edge of a contaminant plume, (b) hydrolysis modeling of methyl chloroform, and (c) inverse modeling.

Leading Edge of a Contaminant Plume in Groundwater

The term L is the length of the contaminant plume. Some portion of L , ΔL , is due to longitudinal dispersion. If the groundwater seepage velocity is u and the retardation factor for the contaminant in question is R , so that the contaminant transport velocity is u/R , then the release date, t , is estimated as

$$t = (L - \Delta L) \frac{R}{u}. \quad (1)$$

The longitudinal dispersion can be estimated as

$$\Delta L = 2\sqrt{\frac{Dt}{R}} = 2\sqrt{\frac{\alpha_L ut}{R}} = 2\sqrt{\alpha_L(L - \Delta L)} \cong 2\sqrt{\alpha_L L} \quad (2)$$

where D is the coefficient of hydrodynamic dispersion, α_L is the longitudinal dispersivity, and molecular dispersion is neglected. The factor of two is included because this appears as part of the characteristic length scale in two- and three-dimensional analytical solutions. The approximate solution for ΔL , for large L , is

$$\Delta L \cong 2\sqrt{\alpha_L L} - 2\alpha \cong 2\sqrt{\alpha_L L} \quad (3)$$

and

$$t = \left(\frac{R}{u}\right)(L - 2\sqrt{\alpha_L L}) \quad (4)$$

which illustrates the importance of correcting for longitudinal dispersion as it decreases with the length of the plume. The groundwater seepage velocity and retardation is expressed as:

$$u = \frac{KI}{\theta_c} \quad (5)$$

and

$$R = 1 + \frac{\rho_b K_d}{\theta_c} \quad (6)$$

where K and I is the hydraulic conductivity and gradient over the plume length, respectively, θ_e is the effective porosity or interconnected pore space of the aquifer, ρ_b is the aquifer material dry bulk density, and K_d is the adsorption distribution coefficient. K_d is often expressed as

$$K_d = K_{oc} f_{oc} \quad (7)$$

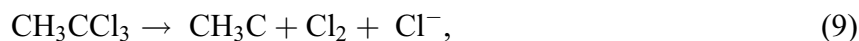
where K_{oc} is the distribution coefficient for partitioning of the solvent between water and organic carbon and f_{oc} is the fraction organic carbon in the soil. With substitutions, the expression for the elapsed time since a release to groundwater becomes

$$t = \left(\frac{\theta_e}{I K_I} \right) \left(1 + \frac{\rho_b K_{oc} f_{oc}}{\theta_e} \right) (L - 2\sqrt{\alpha L}) . \quad (8)$$

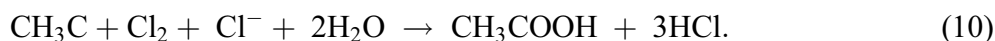
The contaminant plume length is related to the source term, groundwater velocity, and contaminant degradation.

Hydrolysis of Methyl Chloroform

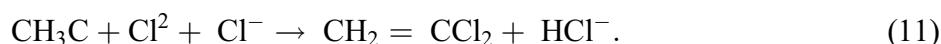
Methyl chloroform (1,1,1-TCA) is unique in that its degradation is hydrolysis driven which can be used to date its release. The method assumes that the rate of chemical hydrolysis of methyl chloroform to acetic acid is known, as is the rate of the elimination reaction to form 1,1-dichloroethylene (1,1-DCE). Other assumptions include that the hydrolysis rate and groundwater temperature are constant, the biodegradation of TCA and 1,1-DCE and the effects of chromatographic separation are insignificant, and that different volatilization rates on the DCE/TCA ratio are negligible. Given these assumptions, the reactions describing the abiotic degradation of methyl chloroform begin as



which is followed by a substitution reaction yielding hydrochloric acid and acetic acid (CH_3COOH) as



Alternatively, the hydrogen can be eliminated to yield DCE (CCl_2) as



These reactions are considered to be first order and temperature dependent. As a consequence, the reaction can be described by the general form of the Arrhenius equation to describe the temperature dependence of the rate of methyl chloroform degradation where the first-order rate constant for TCA (k) is

$$k = A e^{-E_a/RT} \quad (12)$$

where A is the Arrhenius constant; E_a is the activation energy, estimated from laboratory data as 8.7×10^{13} s and 122.8 kJ/mol-°K respectively; R is the universal gas constant (8.3145×10^{-3} kJ/mol-K); and T is temperature (°K). The rate constant for the abiotic degradation of TCA is equal to the sum of the individual rate constants in the substitution and elimination reactions as

$$k = k_s + k_e \quad (13)$$

and

$$[TCA] = [TCA_{(t=0)}] e^{-kt} \quad (14)$$

and

$$[DCE] = \frac{k_e}{k} [TCA_{(t=0)}] (1 - e^{-kt}) \quad (15)$$

where t is time and the molar values of TCA and DCE are bracketed. Equations (14) and (15) solve for t as

$$t = \frac{1}{k} \ln \left(1 + \frac{k[DCE]}{k_e[TCA]} \right). \quad (16)$$

In Eq. (16), t is the estimated time that methyl chloroform entered the groundwater (i.e., without accounting for the time required to migrate through the vadose zone) and is obtained by substituting a single measured value for the molar ratio of $[DCE]/[TCA]$ and groundwater temperature or by substituting time series field measurements. The field estimate of the abiotic rate constant for k is estimated by plotting time series measurements.

When TCE is present and its biodegradation is significant, the *cis*-1,2 dichloroethene (*cis*-1,2 DCE) concentration from this process is approximately two orders of magnitude greater than the 1,1-DCE concentration. Since a small amount of TCE biodegrades to 1,1-DCE relative to the concentration of *cis*-1,2 DCE, this reaction usually affects the 1,1-DCE/TCA ratio only slightly.

Inverse Modeling

Inverse modeling is used to determine the historical distribution of observed contamination, identify a contaminant source, and/or to reconstruct the release history from a known source (Morrison 1999; Michalak and Kitanidis 2003, 2004; Clement 2011). Inverse models include techniques used to determine (1) the location and magnitude of a steady-state point source (Sciortino et al. 2000), (2) the addition of temporal variables to describe a source term(s), (3) the location or time of release of instantaneous point sources, and (4) the use of a function estimate to characterize the historical contaminant distribution, source location, or release history using either a deterministic or stochastic approach (Woodbury et al. 1998; Alapati and Kabala 2000; Aral et al. 2001; Neupauer and Wilson 2002; Butera and Tanda 2003; Morrison 2014). In stochastic approaches to the solution of inverse problems, the unknown parameters are described through probability distributions where the estimated uncertainty is recognized and its importance is often determined, in contrast to deterministic approaches, where a single value is acquired for the unknown parameters (Michalak and Kitanidis 2003).

The development of stochastic approaches where parameters are viewed as a jointly distributed random field is one means of accounting for the uncertainty in contaminant concentration estimates, release history, and release history in a statistical manner, especially if the uncertainty associated with the estimate is quantified (McLaughlin and Townley 1996). The application of inverse models to identify the source of a contaminant release or source loading is nonunique (*equifinality*) with a potentially large degree of uncertainty (Michalak 2001).

Conclusion

Numerous forensic techniques are available to identify the source of a contaminant release and/or bracket when it occurred. Wherever possible, the use of multiple corroborative forensic evidence should be considered in order to establish the most accurate estimate of the origin and date of a contaminant release into the environment.

Cross-References

► [Dendrochronology](#)

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Hydrothermal Ores (Thermochronology)

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Synonyms

[Hydrothermal mineral deposits](#); [Hydrothermal mineralization](#)

Definition

Hydrothermal ores are metal-rich mineral aggregates precipitated directly from hot aqueous solutions circulating through the upper part of the crust. The terms “ore” and “mineral deposit” are economic geology expressions that refer to a mass of rock which contains metals at economically extractable grade. The applicability of these terms can fluctuate as a function of metal market prices, availability of subsidy, or technological conditions.

Introduction

Understanding of the origin of hydrothermal ore deposits requires accurate knowledge about the source and interaction of five important components: heat, fluids, ligands, metals, and permeability. The combination of these factors might provide the conditions necessary for the formation of hydrothermal mineral deposits, including the (i) presence of hot aqueous solution to dissolve and transport minerals, (ii) presence of interconnected openings in the rock to allow the aqueous solutions to move, (iii) availability of sites for the deposits, and (iv) geochemical reactions that will result in deposition (Barnes 1997).

Hydrothermal fluids can be derived from multiple fluid sources in Earth's crust, and these sources and depositional processes have given rise to a variety of genetic classifications of hydrothermal ore deposits (Pirajno 1992). Magmatic–hydrothermal fluids originate from magmas as they cool and crystallize at various levels of the crust and give rise to porphyry-related Cu–Mo–Au deposits (e.g., Sillitoe 2010), skarn- and greisen-related Sn–W deposits (e.g., Meinert et al. 2005), intrusion-linked iron oxide Cu–Au deposits (e.g., Groves et al. 2010), Pb–Zn–Au–Ag-rich replacement, and epithermal Au–Ag ores (e.g., Hedenquist et al. 2000; Simmons et al. 2005). Metamorphic fluids with aqua–carbonic compositions ($\text{H}_2\text{O} + \text{CO}_2$), liberated during prograde mineral reactions, are generally associated with orogenic or shear-hosted Au deposits (Goldfarb et al. 2005). Saline connate fluids formed during diagenesis have been implicated in the formation of stratiform sedimentary rock-hosted Cu and Mississippi Valley-type Pb–Zn ores (e.g., Hitzman et al. 2005; Leach et al. 2005). Seawater circulating through the oceanic crust in the vicinity of active ridges and vented onto sea floor as black smokers forms Cu–Zn-dominated volcanic massive sulfide (VMS) or Zn–Pb-dominated sedimentary exhalative (SEDEX) deposits (e.g., Franklin et al. 2005). Circulation of near-surface meteoric waters can dissolve, transport, and redeposit metals, giving rise to different

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sedimentary rock-hosted deposits such as a variety of uranium ores (e.g., Cuney 2010). The establishment of distinct and well-based genetic hypotheses for several distinct hydrothermal ore deposits remains complicated or poorly understood. For example, multiple fluid sources were proposed for the well-studied Carlin-type Au deposits, including the involvement of magmatic fluid (Sillitoe and Bonham 1990), metamorphic and meteoric sources (Muntean et al. 2011), and a model involving deeply sourced magmatic and metamorphic fluids combined with convecting meteoric water resulting in the dissolution and transport of gold from different locations in the crust (Cline et al. 2005).

Accurate knowledge about the sources of heat that exert a major control on fluid circulation and metal solubility is a key factor to understanding the formation of hydrothermal mineralization. Therefore, low-temperature, radiometric thermochronological methods can potentially provide a unique insight into the mechanisms of ore genesis in the upper crust. Thermochronology can constrain the location, timing, and duration of mineralizing processes. It also can elucidate the relative roles of different heat sources such as metamorphism, magmatism, the burial of sediments, or the juxtaposition of high-temperature isotherms against cooler rocks, via rock uplift and exhumation. Furthermore, there is increasing academic and industry interest in improving our understanding of post-mineralization processes, which preserve or destroy ore deposits and their overlying rocks. Low-temperature thermochronology quantifies the cooling, and potential exhumation histories of rocks, and therefore has useful applications for ore preservation studies, especially when it is combined with other thermochronometric techniques. A comprehensive review of the applications of thermochronology to the study of porphyry ore deposits has been provided by McInnes et al. (2005). This entry presents descriptions and examples of thermochronological methods that have been applied to reveal various types of hydrothermal ore depositional environments.

Dating Hydrothermal Events

Temperature-sensitive radiometric dating techniques can be utilized very efficiently for deciphering the timing and duration of mineralization processes. Additionally, because each low-temperature thermochronometer characterizes a different range of temperatures, the application of multiple thermochronologic techniques is invaluable in constraining the time–temperature history of ore deposition. When thermochronometers are combined with geochronometers (e.g., U–Pb dating, Re–Os dating, or Rb–Sr dating), they can be utilized to the best advantage and can elucidate many aspects of ore deposit genesis, including intrusive emplacement, ore deposition, alteration processes, overprinting or retrograde hydrothermal events, erosion, and weathering.

Ar–Ar dating is regularly used to determine the timing of mineralization processes, as K-bearing minerals often form as part of the ore mineral paragenesis or as alteration minerals. Biotite, K-feldspar (adularia), muscovite, and alunite are commonly dated from various hydrothermal deposit types, including porphyry Cu–Mo–Au, epithermal Au–Ag, orogenic or shear-hosted Au, or Mississippi Valley-type Pb–Zn mineralization systems. The Ar–Ar step-heating technique can yield both the minimum age of host-rock crystallization (high-temperature steps) and the timing of younger thermal events (lower-temperature steps) on a single K-feldspar. It is therefore very effective to determine the timing of retrograde hydrothermal heating events and to estimate the cooling rates of the mineralizing systems. Recently, there has been increasing interest in dating sulfide minerals where K is present in mineral or fluid inclusions, as sulfides generally have very low diffusivity for Ar, and hence protects the inclusions from resetting. Promising examples include

concordant Ar–Ar ages that have been obtained for fluid inclusion-rich sphalerites from Fankou Pb–Zn deposit (Qiu and Jiang 2007) and for mica-bearing pyrites from Archean Kanowna Belle Au deposit (Philips and Miller 2006).

Fission-track thermochronology can be used for absolute dating; however, this is only possible for samples that have cooled rapidly and have remained undisturbed at, or close to, the surface since formation. Due to complicated thermal histories and because of the relative lack of apatite in hydrothermal ore paragenesis, fission-track analysis is rarely used for direct dating of hydrothermal systems. More commonly, apparent ages are obtained which are used for the reconstruction of the postmineral thermal history (cooling, exhumation, preservation).

(U–Th)/He dating of hydrothermal ore deposits has gained more and more focus with the development of new (U–Th)/He chronometers which have closure temperatures overlapping with hydrothermal conditions and which use minerals commonly occurring in hydrothermal ore paragenesis. As examples, concordant (U–Th)/He were obtained for epidote and garnet from skarn mineralization (Nicolescu and Reiners 2005), for specular hematite (Lippolt et al. 1993), for fluorite from the La Azul fluorspar deposit (Pi et al. 2005), and for titanite (Reiners and Farley 1999) and magnetite (Blackburn et al. 2007), respectively.

Mapping Thermal Footprints Related to Hydrothermal Fluid Flow

One of the main challenges facing exploration geologists investigating subsurface hydrothermal mineralization is the identification of the far-field expressions (footprints) of hydrothermal systems (Kelley et al. 2006). Traditionally, research on the footprints related to hydrothermal fluid flow focuses on mineralogical alteration products (i.e., visual alteration) and on the patterns of primary or secondary lithogeochemical dispersion halos, which are the result of progressive fluid–rock interaction. However, often these proximal footprints are subtle or are partially restricted to main fluid flux zones, which make it difficult to identify and map out concealed hydrothermal ores (Fig. 1). A commonly neglected aspect of hydrothermal fluid flow is the resultant heat transfer to rock within and around the fluid conduit. Heating is a product of advection (flow of heated fluid mass) and diffusion (conduction of heat through a fluid or rock mass). A thermal halo should develop around all hydrothermal deposits; the size of the halo being a function of the duration of hydrothermal flow, the magnitude of the fluid flux, the temperature difference between the thermal fluids and the country rock, and the size, shape, and density of the fluid conduits (Cathles et al. 2006). Recent studies demonstrate that these thermal haloes can be detected at distances up to several hundred meters around hydrothermal mineralization when studying stable isotope fractionation or the rate of annealing of fission tracks within the wall rock minerals (Arehart and Donelick 2006; Hickey et al. 2007; Barker et al. 2013). The extent of fission-track resetting is a nonlinear function of the duration and magnitude of the heating. As the magnitude and duration of conductive heating decreases outward from the hydrothermal fluid conduit, fission tracks close to the conduit will be reset to a greater extent than those farther away. The pattern of fission-track resetting will largely reflect the period and temperature of the fluid flow event that induced the conductive heating pulse.

Dating by apatite fission tracks (AFT; which reset as apatite is heated above 60 °C; Donelick et al. 2005), in combination with the apatite (U–Th)/He dating method (closure temperature ~70 °C; Ehlers and Farley 2003), is the most widely utilized thermochronometer for mapping low-temperature thermal fronts associated with channelized fluid flow. Studies of sedimentary rock-hosted gold deposits in the northern Carlin trend (USA) suggest that single-conduit focusing of 200–240 °C ore fluids over a relatively short duration ($\sim 10^4$ years) is capable of completely

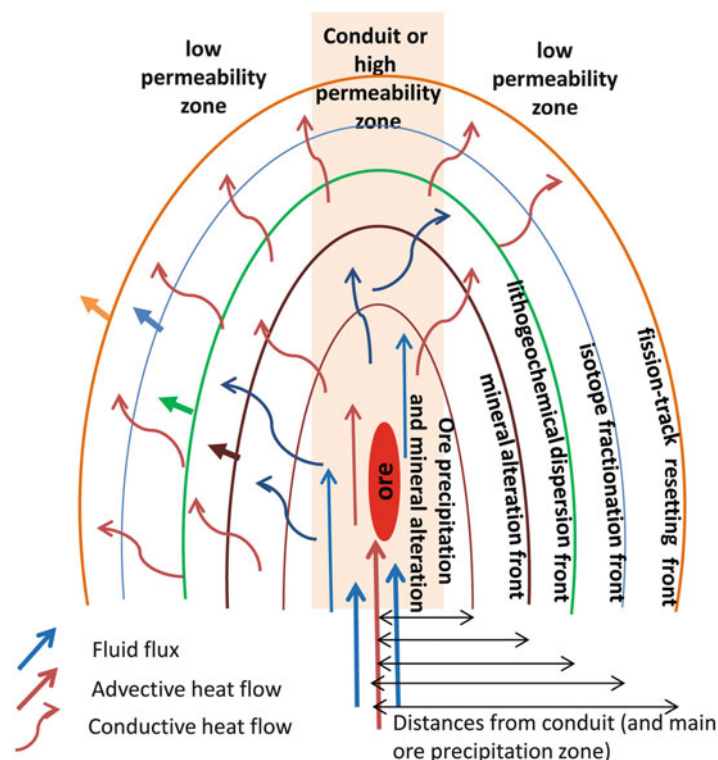


Fig. 1 Idealized representation of hydrothermal and thermal footprint zones related to single fluid flow conduits in hydrothermal ore systems

resetting AFT ages at a distance of ~ 325 m, while a ~ 10 % change in AFT age relative to background occurs at a distance of ~ 800 m (Hickey et al. 2014). In systems where conduits are close enough for conductive thermal fronts to interact (double-sided slab heating), the 10 % resetting and total resetting fronts are able to completely propagate across slabs $\sim 1,100$ m (~ 10 % change in AFT ages relative to background) and ~ 700 m (complete resetting of AFT ages) wide, respectively (Hickey et al. 2014).

Genetic Aspects of Hydrothermal Mineralization: Possible Heat Sources

Since the stability of metal–ligand complexes is primarily controlled by temperature and generally enhanced by elevated temperatures, it is clear that the role of heat is critical during the leaching, transport, and deposition of metals by hydrothermal fluids. Generally, strong thermal gradients present the ideal conditions for the generation of high-grade magmatic hydrothermal ores, whereas more diffuse mineralization haloes would be expected for more slowly cooled igneous intrusions. Moreover, many authors have discussed the significance of thermally driven fluid flow during the formation of basin-related hydrothermal ore deposits. Therefore, the application of thermal history modeling to investigate possible heat sources and their gradients represents a powerful tool for understanding genetic aspects of ore deposition.

As illustrated by a case study from Eastern Rhodopes, Bulgaria (Fig. 2), Márton (2009) demonstrated that sufficient heat accumulated from multiple sources to sustain an ore-deposit-forming hydrothermal system. The relative roles of different heat sources resulting from metamorphism, magmatism, the burial of sediments in environment with high geothermal gradients, or the

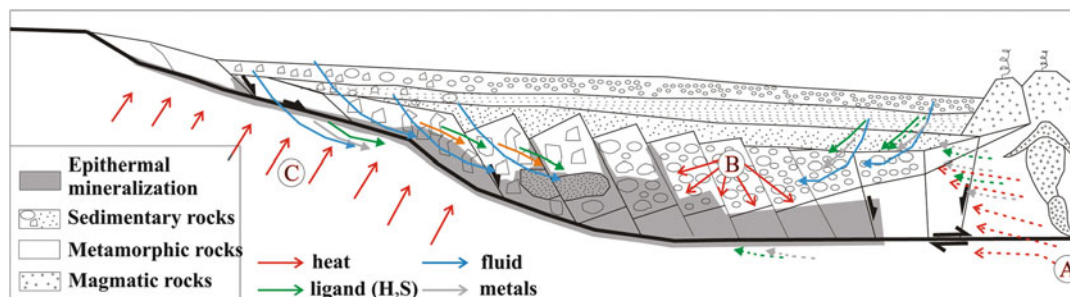


Fig. 2 Model illustrating various possible fluids (blue arrows), metals (gray arrows), ligands (green arrows), and heat (red arrows; A magmatic, B burial, C high geothermal gradient) (sources associated with the formation of sedimentary rock-hosted gold mineralization from Eastern Rhodopes, Bulgaria (after Márton 2009))

juxtaposition of high-temperature isotherms against cooler rocks via rock uplift and exhumation were quantified using multiple thermochronometers and applying appropriate sampling profiles which consider the various geological processes.

Preservation and Exhumation of Hydrothermal Ore Deposits

Hydrothermal ore deposits that form in the shallow crust (<5 km) are frequently obliterated by erosion and reworking, particularly if they form in environments that are being exhumed (Wilkinson and Kesler 2007). The probability of exposure of a hypogene subsurface ore is clearly a function of the depth at which it formed and the rate at which it is exhumed toward the surface. Therefore, concealment of shallow, epithermal ore deposits by post-mineralization sedimentation represents a convenient way to preserve them for a longer time (Fig. 3). Thermal history modeling provides a means to quantify the timing, magnitude, and duration of heating and cooling events that occurred during the tectonic evolution of an area and is useful to establish a plausible exhumation history. In this context, low-temperature thermochronological data can be used as an exploration tool for the identification of shallow ore deposits in the crusts. Favorable targets can be represented by time–temperature results that corroborate ore emplacement depth, exhumation rate, and age-distribution characteristics.

Márton et al. (2010) integrated the results of $^{40}\text{Ar}/^{39}\text{Ar}$ step-heating analyses of hornblende, muscovite, biotite, and adularia, along with zircon and apatite fission-track analyses from upper and lower plate rocks of the Kesebir–Kardamos metamorphic core complex from the Eastern Rhodopes, Bulgaria, where Oligocene epithermal sedimentary rock-hosted Au mineralization was formed in upper plate position in close spatial relationship to detachment faults. The resulting thermal history models for the upper plate show that ore formation was followed by continuous sedimentation until ~33–30 Ma, which may account for the fact that the mineralized zones were preserved, and the exhumation of these deposits suddenly started with the onset of horst–graben formation at ~33–30 Ma. The steep, post-mineralization normal faults played a key role during the exhumation of the deposit representing the bounding structures of the exhumed gold deposits. Therefore, structural mapping should focus not only on the low angle detachment faults, which might be genetically related to ore formation, but also on post-mineralization faults, which exhumed the deposits.

LA–ICP–MS apatite U–Pb dating and fission-track thermochronology were also applied to determine the preservation potential of magnetite–apatite deposits in the Luzong and Ningwu

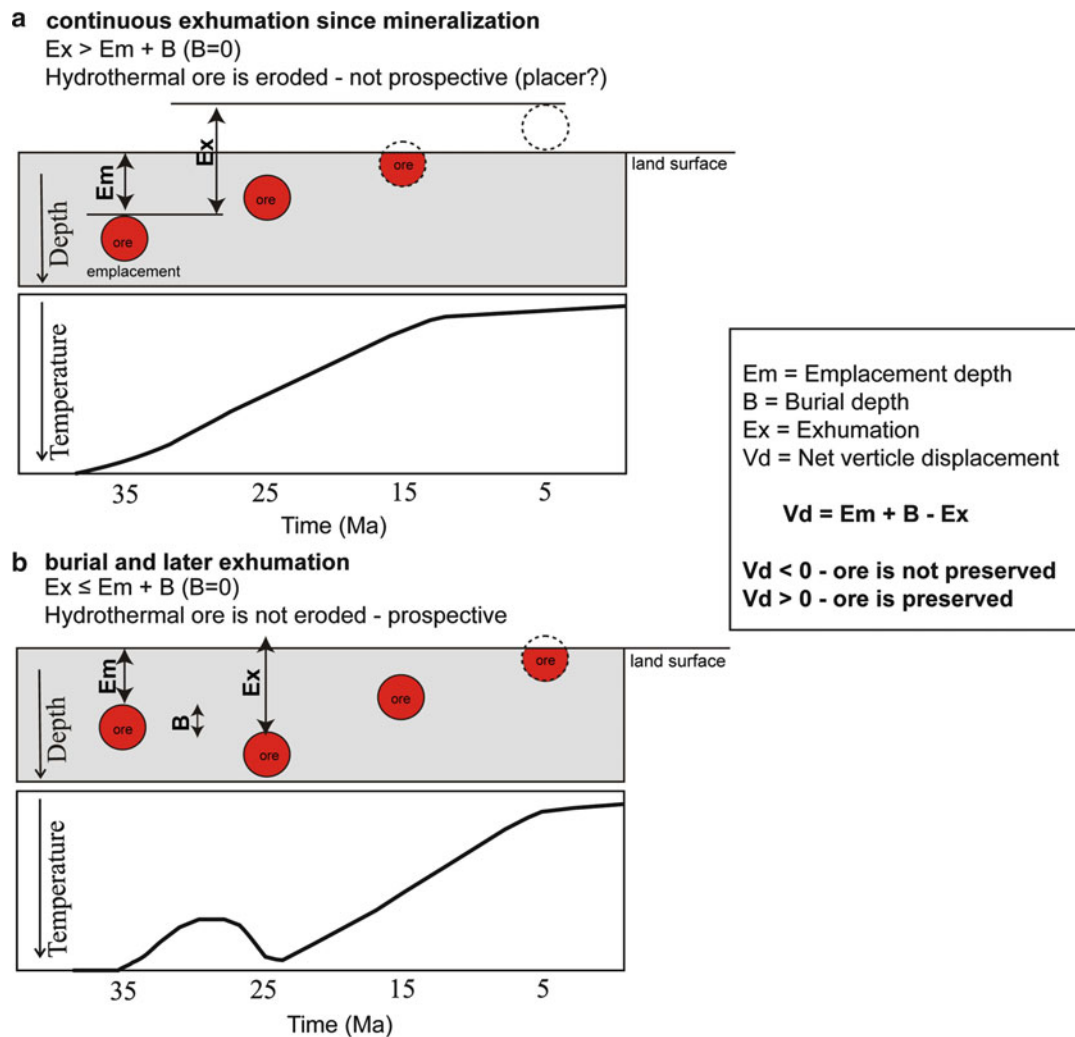


Fig. 3 Relationships between emplacement depth, erosion history (*upper panels*), and time–temperature evolution (*lower panels*) during the exhumation history of epithermal Au deposits (*red dots*). (**a**) The area experienced continuous exhumation since hypogene ore deposit formation, and the ore deposit was eroded in the past making the area unfavorable for present-day exploration, although potential supergene/placer ores might form in related river catchment zones. (**b**) After ore formation the early history of the area includes a burial period and subsequent exhumation. This scenario renders the area favorable for present-day ore exploration

volcanic basins, eastern China (Liu et al. 2014). Results suggest that although the metallogenic conditions of both basins were similarly favorable for the formation of the of magnetite–apatite deposits, the Luzong basin had better preservation potential and therefore more promise for development of the magnetite–apatite deposits.

Quantifying Fault Displacement in Mineralized Zones

The identification of postmineral faults and the reconstruction of fault displacement have major implications for the exploration of ore deposits, as it can reveal the tilting history of an explored area and allow identification of missing (faulted) portions of an ore deposit.

Under thermal steady-state conditions, where isotherms are fixed relative to the surface, changes in time–temperature profiles from a certain sampling profile reflect the movement of a sample with respect to the surface. In this situation, low-temperature thermochronometers can be used to constrain patterns of footwall denudation associated with fault-array evolution. Samples collected along fault-perpendicular footwall transects can be used to construct age versus elevation profiles that may constrain the timing of fault displacement as well as the magnitude and rate of footwall denudation. Vertical fault displacement and erosion must be sufficient to exhume the partial retention zone; otherwise, the fault displacement will not be resolved. Samples at higher structural levels pass through this temperature zone earlier than those located at lower levels, resulting in an age–elevation profile in which apparent cooling ages decrease linearly with elevation. For a purely vertical transect, the slope of the age–elevation profile defines the rate of footwall denudation and may constrain the timing of fault activity.

A well-documented example of postmineral fault displacement was provided at the Chuquicamata Cu–Mo deposit, where a significant portion of the western side of the ore body was dislocated by post-mineralization motion along the West Fault, a major N–S strike-slip feature that cuts through Northern Chile (McInnes et al. 1999). U–Th/He and fission-track data collected on both sides of the West Fault documented a clear offset, revealing the vertical component of displacement. Younger ages in the hanging wall (to the west) indicate that it has been exhumed relative to the footwall, and there has been ~600 m of vertical displacement along the West Fault. The results suggest that the missing portion of the Chuquicamata Cu–Mo deposit was not yet eroded during tectonic uplift and denudation and should still be present at an elevation of 3,600 m, 25–35 km along the strike (sinistral) of the current open pit at Chuquicamata.

Summary

Thermochronologic data provides important constraints on the role of different processes in the formation, preservation, and exhumation of hydrothermal ore deposits. Thermochronologic results integrated in time–temperature paths permit an assessment of the timing, magnitude, and duration of hydrothermal mineralization events in relation to magmatic, metamorphic, and sedimentary processes. The source of heat and the thermal-gradient footprints related to hydrothermal systems can be mapped using diverse thermochronometers. Resulting models of thermal history offer a quantitative framework for the evaluation of ore preservation potential of an area and for the economic assessment of different tectonic units from a mineralized belt.

Cross-References

- [Apatite](#)
- [Ar–Ar and K–Ar Dating](#)
- [Exhumation \(Thermochronology\)](#)
- [Fault Zone \(Thermochronology\)](#)
- [Fission Track Dating and Thermochronology](#)
- [Hydrothermal Events \(Rb–Sr\)](#)
- [Igneous Rocks \(K–Ar\)](#)
- [Metamorphic Terranes \(K–Ar/Ar–Ar\)](#)
- [Minerals \(Ar–Ar\)](#)

- [Structural Fabrics \(K–Ar/Ar–Ar\)](#)
- [Thermochronology, Detrital Zircon](#)
- [Thermochronology, Landform Evolution](#)
- [Uranium-Lead Dating](#)
- [Uranium-Lead, Ore Deposits](#)
- [U–Th:He Dating](#)
- [Volcanic Rocks Ar–Ar](#)
- [Volcanogenic Sedimentary Rocks \(K/Ar, 40Ar/39Ar\)](#)
- [Zircon](#)

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Uranium Series, Opal

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Synonyms

U-series disequilibrium; $^{230}\text{Th}/\text{U}$ ages; Opaline silica

Definition

Uranium series dating. A geochronological method that uses intermediate decay products in the ^{238}U or ^{235}U radioactive decay chains to measure the length of time required to reach the current state of radioactive disequilibrium from an initial condition.

Opal. Amorphous or only partially crystalline hydrated silicon dioxide ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) precipitated from aqueous solutions in near-Earth-surface environments.

Mineralogy and Geochemistry of Opal

Opal is a common mineraloid found near the surface of the Earth that consists of silica containing nonstructural water ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Opal typically forms by precipitation of colloidal silica from silica-saturated aqueous solutions in response to decreases in temperature, neutralization of alkaline solutions, increases in salinity, or evaporative concentration. Sedimentation of colloidal microspheres (<500 nm) results in deposits of amorphous silica gel. Subsequent dewatering and diagenesis causes gels to solidify and gradually increase their structural ordering. Water contents typically range between 0.5 % and 10 % and tend to decrease with increasing crystallinity.

Opals have been distinguished on the basis of their degree of crystallinity determined by x-ray diffraction (Jones and Segnit 1971). These include amorphous opal (opal-A), disordered α -cristobalite with α -tridymite stacking (opal-CT), and more ordered α -cristobalite with minor tridymite stacking (opal-C). Progressive increases in the degree of ordering from opal-A through chalcedony (Fig. 1) have been observed in response to increasing temperature as well as increasing age (Kano 1983; Herdianita et al. 2000; Neymark et al. 2003).

Opal is most common in volcanic or sedimentary settings and is associated with alteration or weathering of silicate rocks. Materials display a wide range of colors (known as play of color), textures, opalescence, and luminescent properties. Opal is also classified as gem opal (also precious or noble opal) or common opal (also, potch opal) based on its ability to diffract visible light into a spectral array of colors (Smith 1998). Play of color is the property observed when well-sorted (~ 150 – 250 μm) opal microspheres are clustered into ordered arrays (Jones et al. 1964; Darraugh et al. 1965). Common opal forms when microspheres are less well sorted and cluster without orderly packing.

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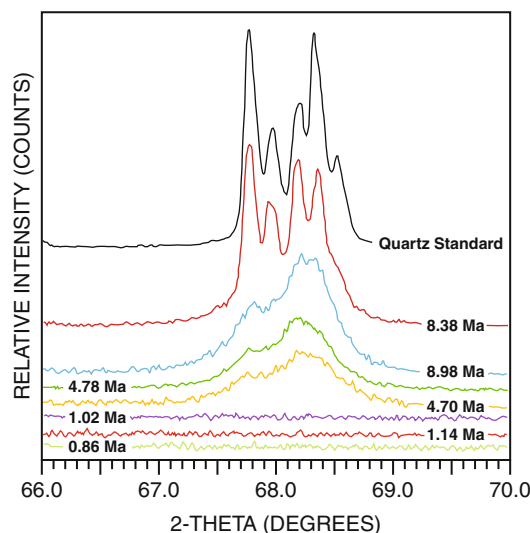


Fig. 1 Relative x-ray intensity data over part of the diffraction pattern between 66° and 70° 2-theta for subsamples of opal dated by $^{207}\text{Pb}/^{235}\text{U}$ from a single subsurface secondary mineral crust at Yucca Mountain, Nevada. Data show progressive increases in peak structure and intensity with age until older subsamples show patterns similar to the quartz standard. Modified after Fig. 6 of Neymark et al. (2003)

Gailliou et al. (2008) documented the geochemistry of a variety of gem and common opals from various localities around the world. Typical impurities (elements with concentrations $>500 \mu\text{g/g}$) include Al, Ca, K, Mg, Fe, and Na, whereas common trace elements ($<500 \mu\text{g/g}$) include Ba, Sr, Rb, Mn, Ti, U, and Nb. Gailliou et al. (2008) found that the trace element chemistry in opal can be linked to that of the host rock, particularly for rare earth elements (REE), allowing geochemical fingerprinting of gem opals to their geographic origin. The most pertinent compositional data for the purposes of dating opal are concentrations of U relative to Th (for $^{230}\text{Th}/\text{U}$ dating) and U relative to Pb (for U–Pb dating). U concentrations in the 76 analyses from 13 localities reported by Gailliou et al. (2008) range from 0.01 to 131 $\mu\text{g/g}$, although U concentrations from hundreds to thousands of $\mu\text{g/g}$ have been reported from other localities (Ludwig et al. 1980; Paces et al. 2010, supplement). Like REE, tetravalent U and Th are largely insoluble in aqueous solutions; therefore, U/Th ratios in opal can remain similar to values found in host rocks (typically 0.1–0.5). However, hexavalent U can be highly soluble in oxidizing groundwater, especially as the uranyl ion (UO_2^{2+}) complexed with other anions such as CO_3^{2-} (Langmuir 1978; Porcelli 2008). Natural oxidizing, bicarbonate-rich surface water and groundwater commonly have U concentrations ranging from 0.1 to 20 $\mu\text{g/L}$, whereas Th and Pb remain insoluble (typically <0.02 and $<0.2 \mu\text{g/L}$, respectively). Consequently, opal formed under oxidizing conditions has the potential to have U/Th and U/Pb ratios favorable for dating due to lack of ^{230}Th or Pb incorporated during formation.

U-Series Disequilibrium Dating of Opal

Several geochronometers are available within the U-decay chain and rely on the growth or decay of various intermediate decay products including ^{234}U , ^{230}Th , ^{226}Ra , ^{231}Pa , and several shorter-lived products (see entry on “► U-series Dating”). The only two chronometers using intermediate decay products that have been applied to opal include the $^{230}\text{Th}/\text{U}$ method with a working range of about 0 to 400,000 years (400 ka) and the model $^{234}\text{U}/^{238}\text{U}$ method with a working range up to about

1,200 ka. Older opals (>100 ka) have been dated using U–Pb methods, although issues related to initial $^{234}\text{U}/^{238}\text{U}$ disequilibrium must be considered.

Initial Investigations of Opal as a Geochronometer

The ability for silica gel to concentrate U from groundwater was recognized during the late 1970s in uraniferous silica related to uranium ore deposits (Zielinski 1977, 1980). Experiments with uranium-bearing silica-saturated solutions indicated that dried silica gels contained U concentrations that were 400–1,000 times higher than U concentrations in source water (Zielinski 1980). U–Pb isotopic compositions were also investigated to evaluate the possible use of uraniferous opal and chalcedony as geochronometers. Ludwig et al. (1980) found that opal-CT with U concentrations of 84.5–3,940 $\mu\text{g/g}$ at Spor Mountain, Utah, USA, had low common Pb contents and high retention of U-daughter products. Two distinct $^{207}\text{Pb}^*/^{235}\text{U}$ age intervals were determined (where the asterisk denotes only the radiogenic ^{207}Pb derived from in situ decay of parental ^{235}U , obtained after subtraction of “common,” non-radiogenic Pb): 4.8–3.4 Ma for five analyses hosted in rhyolites dated at 39–6 Ma and 16–13 Ma for five analyses hosted in the Beryllium Tuff Member of the Spor Mountain Formation dated at 21 Ma. Furthermore, $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratios for most analyses were consistent with samples having initial $^{234}\text{U}/^{238}\text{U}$ activity ratios (AR) in the range typically expected for thermal waters in young volcanic terrains. Based on results of HCl leaching experiments, clustering of $^{207}\text{Pb}^*/^{235}\text{U}$ ages and $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ consistent with expected initial $^{234}\text{U}/^{238}\text{U}$ AR values, Ludwig et al. (1980) concluded that Spor Mountain opals approximated a closed system for U and its daughter products and that U–Pb dating of opal as young as ~1 Ma was possible.

Szabo and Kyser (1985, 1990) found that uraniferous opal, identified by its bright yellow-green fluorescence under short-wavelength ultraviolet light, had elevated U concentrations (15–58 $\mu\text{g/g}$) and low Th concentrations ($^{230}\text{Th}/^{232}\text{Th}$ AR = 150–470) in subsurface veins and fracture coatings hosted in drill cores from 13-Ma volcanic rocks at Yucca Mountain, Nevada. The characteristic fluorescence coloration has been attributed to activation caused by trace amounts of U (Hanchar 1999). Attempts to obtain U-series dates for those opals by alpha-spectrometry were unsuccessful, despite the presence of U-series disequilibrium in 3 of 4 samples (see “► U-series Dating,” for description of method). Alpha-spectrometry methods required large samples (up to a gram or more) which were homogenized by pulverizing and heated for 8 h prior to digestion and U–Th purification. More recent investigations using isotope dilution thermal ionization mass spectrometry (ID-TIMS) on much smaller samples of similar opal from the same site suggest that the alpha-spectrometry data likely represent mixtures of younger and older material and have little true age meaning (see discussion of “Vadose-Zone Hyalitic Opal” below).

U-Series Dating of Pedogenic Opal

By the mid- to late 1990s, U-series dating by ID-TIMS was applied to pedogenic deposits in southern Nevada with a focus on opaline silica components of complex, laminated clast rinds (Ludwig and Paces 2002). Pedogenic opal in these soils typically forms hard, opaque, light tan- to brown-colored layers that contrast sharply with softer, lighter-colored carbonate. Scanning electron microscopy (backscatter imaging and energy-dispersive x-ray fluorescence) showed that rind layers can consist of dense, silica-rich material alternating with more porous calcite, as well as layers containing intimate mixtures of calcite and silica at very fine scales. Dilute acid leaching experiments on clast rinds demonstrated that U is enriched in the residual silica-rich phase relative to easily leached carbonate phase. This causes problems when attempting to date complex pedogenic material by the so-called leach/leach and leach/residue methods (Schwarcz and Latham 1989; Bischoff and Fitzpatrick 1991; Luo and Ku 1991) because both ^{230}Th and ^{234}U can be implanted from the higher-

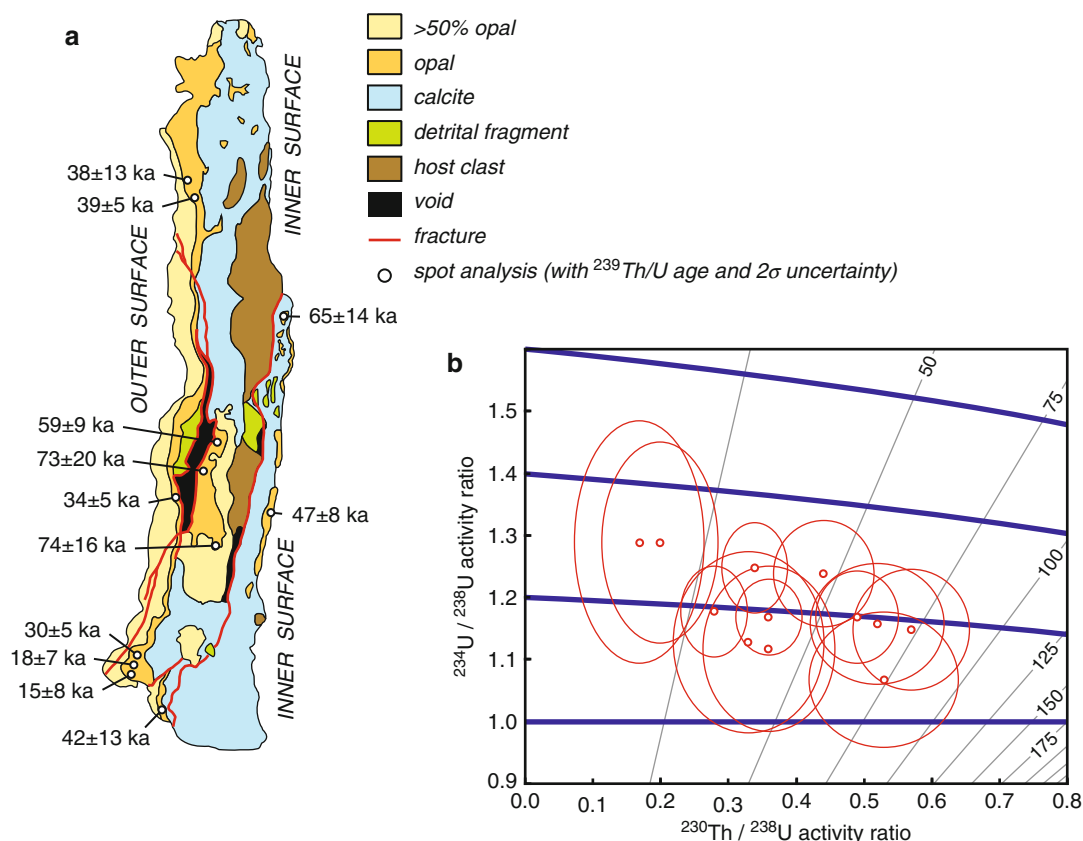


Fig. 2 U-series dating results for a pedogenic rind off an alluvial clast from the Calico Mountains, California. **(a)** Cross-sectional map showing the distribution of carbonate- and opal-rich layers and ~30- μm -diameter spots analyzed by secondary ion mass spectrometry. **(b)** Th–U isotope evolution plot showing data (small circles) and 95 % confidence level uncertainties (error ellipses) for spots shown on rind in **(a)**. Ages range from 15 to 74 ka (isochrons shown as steeply sloping light gray lines at 25-ka intervals) with relatively uniform initial $^{234}\text{U} / ^{238}\text{U}$ activity ratios of ~1.2 (thick, blue, subhorizontal lines) (Modified after Figs. 5 and 6 of Maher et al. (2007))

U silica phase into the lower-U carbonate phase via alpha-recoil. Consequently, unsupported daughter isotopes in the more readily leachable phases are likely to have $^{230}\text{Th} / ^{238}\text{U}$ ratios without clear time significance regardless of whether they are treated as single data points, isochrons, or leach/residue pairs (Ludwig and Paces 2002, p. 495). Those authors concluded that total digestion of thin, opal-rich, detritus-poor layers produced the most reliable analyses with elevated U and $^{238}\text{U} / ^{232}\text{Th}$ values. Reported ages for opal-rich samples ranging from 10^4 to nearly 10^6 years were consistent with internal microstratigraphy within individual clast rinds as well as overall stratigraphic relations for samples from modern and buried horizons.

Maher et al. (2007) further investigated U-series dating of surficial deposits using secondary ion mass spectrometry (SIMS) to probe pedogenic opal at higher spatial resolutions. Primary beam spot sizes of ~30 μm allowed targeting of small, relatively pure authigenic silica with high U concentrations and U/Th ratios (Fig. 2a). This strategy has the benefit of minimizing corrections for initial ^{230}Th associated with detrital components, reducing sample size requirements, eliminating chemical preparation, and allowing evaluation of soil development at microstratigraphic scales (Fig. 2b). However, in order to obtain sufficient secondary ion beams of minor isotopes (^{234}U and ^{230}Th), silica-rich pedogenic cements with U concentrations greater than about 50 $\mu\text{g/g}$ were required for SIMS analyses. In contrast, pedogenic carbonate typically has U concentrations less than 10 $\mu\text{g/g}$. The imprecision caused by low count rates for minor isotopes can be offset by reduced uncertainty

associated with smaller detrital Th corrections. Maher et al. (2007) argued that although TIMS analyses yield higher analytical precisions, ages determined at finer spatial resolutions by SIMS analyses may have greater accuracy, especially for finely layered samples with complex growth histories.

U-Series Dating of Vadose Zone Hyalitic Opal

The need to understand the history of water movement through the unsaturated zone at Yucca Mountain, Nevada, which was intended to host a high-level nuclear waste repository, prompted substantial work with secondary mineral coatings lining fracture footwalls and lithophysal cavity floors. These coatings are dominated by deposits of coarsely crystalline calcite with smaller amounts of water-clear, hyalitic opal (Paces et al. 2001; Whelan et al. 2002). Opal forms small (<1–2 mm), finely layered, glassy hemispheres; globular masses; or thin sheets on calcite substrates. Although both phases precipitated from the same downward-percolating solutions, opal contains U concentrations that are 2–4 orders of magnitude higher than calcite (~5–300 µg/g U versus 0.005–0.04 µg/g U, respectively; Paces et al. 2001). Concentrations of Th are extremely low resulting in $^{230}\text{Th}/^{232}\text{Th}$ AR up to 10^6 . Initial attempts to date whole hemispheres of opal from mineral crust surfaces using ID-TIMS yielded ages ranging between about 40 and >600 ka that showed a suspicious negative correlation with initial $^{234}\text{U}/^{238}\text{U}$ AR (from 6 to 10 for the youngest samples to 1 and 2 for older samples). However, none of the analyses had unsupported ^{230}Th , implying little or no post-depositional uranium mobility. These features, plus an apparent positive correlation between age and sample size, suggested that Yucca Mountain opals do not fit the assumptions of simple, closed-system isotope evolution in an instantaneously deposited layer.

Instead, Neymark and Paces (2000) proposed a conceptual model of continuous deposition where opal precipitated at constant rates over long periods of time up through the present. Samples with finite thickness consist of a mixture of older and younger material that yield isotopic compositions reflecting addition of new layers with elevated $^{234}\text{U}/^{238}\text{U}$ at the same time that U-series compositions of previously deposited layers evolve by radioactive decay. Average ages calculated using continuous deposition equations combined with the typical thickness of 0.1–0.5 mm resulted in estimates of opal deposition rates between about 0.1 and 5.0 µm/ka. These conclusions are consistent with the observation that ages for the outermost mineral layers determined using geochronometers with progressively longer half-lives (i.e., ^{14}C , $^{230}\text{Th}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$) yield discordant, progressively older ages (Fig. 7 of Neymark et al. 2000).

To test the model of continuous deposition of Yucca Mountain opal, two methods of U-series dating at higher spatial resolutions were developed, including SIMS and in situ micro-digestion followed by ID-TIMS analysis (Paces et al. 2004). SIMS analyses utilized a primary oxygen ion beam to sputter metal and oxide ions from ~45-µm-diameter pits across profiles of layered opal hemispheres. Resulting $^{230}\text{Th}/\text{U}$ ages ranged from 34.4 to >300 ka, increasing progressively with depth below the outer surface. Uncertainties were substantially larger than previous ID-TIMS results due to the much smaller signals; however, $^{234}\text{U}/^{238}\text{U}$ versus $^{230}\text{Th}/^{238}\text{U}$ compositions followed trajectories expected for closed-system evolution unlike the scatter observed for whole-hemisphere results (Fig. 7 of Paces et al. 2004). Model $^{234}\text{U}/^{238}\text{U}$ ages ranging between 277 and 1,430 ka were calculated for older layers using the assumption that the average initial $^{234}\text{U}/^{238}\text{U}$ AR determined for spots younger than 200 ka remained uniform over time. Both $^{230}\text{Th}/\text{U}$ and model $^{234}\text{U}/^{238}\text{U}$ ages combined with microstratigraphic depths across two opal hemispheres yielded linear growth rates of 0.58 and 0.69 µm/ka. The second method, in situ micro-digestion, involved exposing the outer surface of hyalitic opal hemispheres to single or sequential HF digestion steps that removed between 1.5 and 3.8 µm of opal per step. Digestions were spiked with a mixed tracer solution of ^{236}U and

^{229}Th and taken to dryness. Because of the high purity of the hyalitic opal, chemical separations were not necessary prior to loading remaining salts onto carbon-doped, single Re filaments. U isotopes were measured by TIMS at lower temperatures prior to measurement of Th isotopes from the same filament at higher temperatures. As expected, the thinner outermost layers yielded younger ages (4.0–11.6 ka), and sequential digestions yielded an average growth rate of $0.68 \pm 0.22 \mu\text{m/ka}$ over the last 37 ka (compared to 0.69 ± 0.07 for the same hemisphere analyzed by SIMS). These investigations confirmed the continuous deposition numerical model proposed earlier and demonstrated that opal in this setting was formed at extremely slow growth rates over very long periods of time.

Subsequent investigations using SIMS analyses at even higher spatial resolution ($\sim 25 \mu\text{m}$ wide by $10 \mu\text{m}$ deep pits) demonstrated similarly slow, continuous growth rates in additional samples of Yucca Mountain hyalitic opal (Fig. 3; Paces et al. 2010). Systematic variations in cathodoluminescence intensity that follows growth banding were shown to be caused by variations in U concentrations from 5.4 to $550 \mu\text{g/g}$. Age-calibrated profiles of U concentrations were shown to correlate with regional climate records over the past 300 ka, indicating a clear chemical response of percolating water to near-surface, climate-driven processes. Nevertheless, the slow and relatively uniform opal growth rates over this time period were used to argue that water fluxes in the deep vadose zone were buffered from the large fluctuations in available surface moisture observed in other climate records in the region.

U-Series Dating of Opal by Laser Ablation ICPMS

Stirling et al. (2000) reported the first U-series analyses of a hyalitic opal from Yucca Mountain using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Those authors were able to obtain uranium isotope compositions in secular equilibrium ($^{234}\text{U}/^{238}\text{U} \text{ AR} = 0.9997 \pm 0.0034$ [$2 \times$ standard error]) as expected for samples of three-million-year-old opal using a 266-nm Nd:YAG laser with a $150\text{-}\mu\text{m}$ -diameter spot size. Significant fractionation of U and Th was observed during initial experiments; however, the degree of fractionation was greatly reduced by changing ionization conditions in the plasma. More recent developments of laser ablation methods have further reduced analytical problems allowing $^{230}\text{Th}/\text{U}$ dating of carbonate, apatite, iron oxides, and silicate glasses with U concentrations as low as a few $\mu\text{g/g}$ (Eggins et al. 2005; Bernal et al. 2005; Grün et al. 2008). Application of these methods to opal in the future is likely to yield reliable ages allowing evaluation of growth rates, environmental conditions, and hydrologic processes associated with a wide variety of near-surface settings.

Summary

Opal is a very common product of secondary silica mobilization in near-surface hydrologic environments. If deposited from oxidizing solutions, it may incorporate high U concentrations with little or no initial ^{230}Th making it an ideal candidate for dating by U-series disequilibrium methods. Under near-surface conditions, opal can retain U-decay products for long periods of time ($> 10^6$ years). Most studies have focused on opal present in soils and thick vadose zones; however, wider recognition of its presence in these and other hydrologic settings will expand its application as a geochronometer.

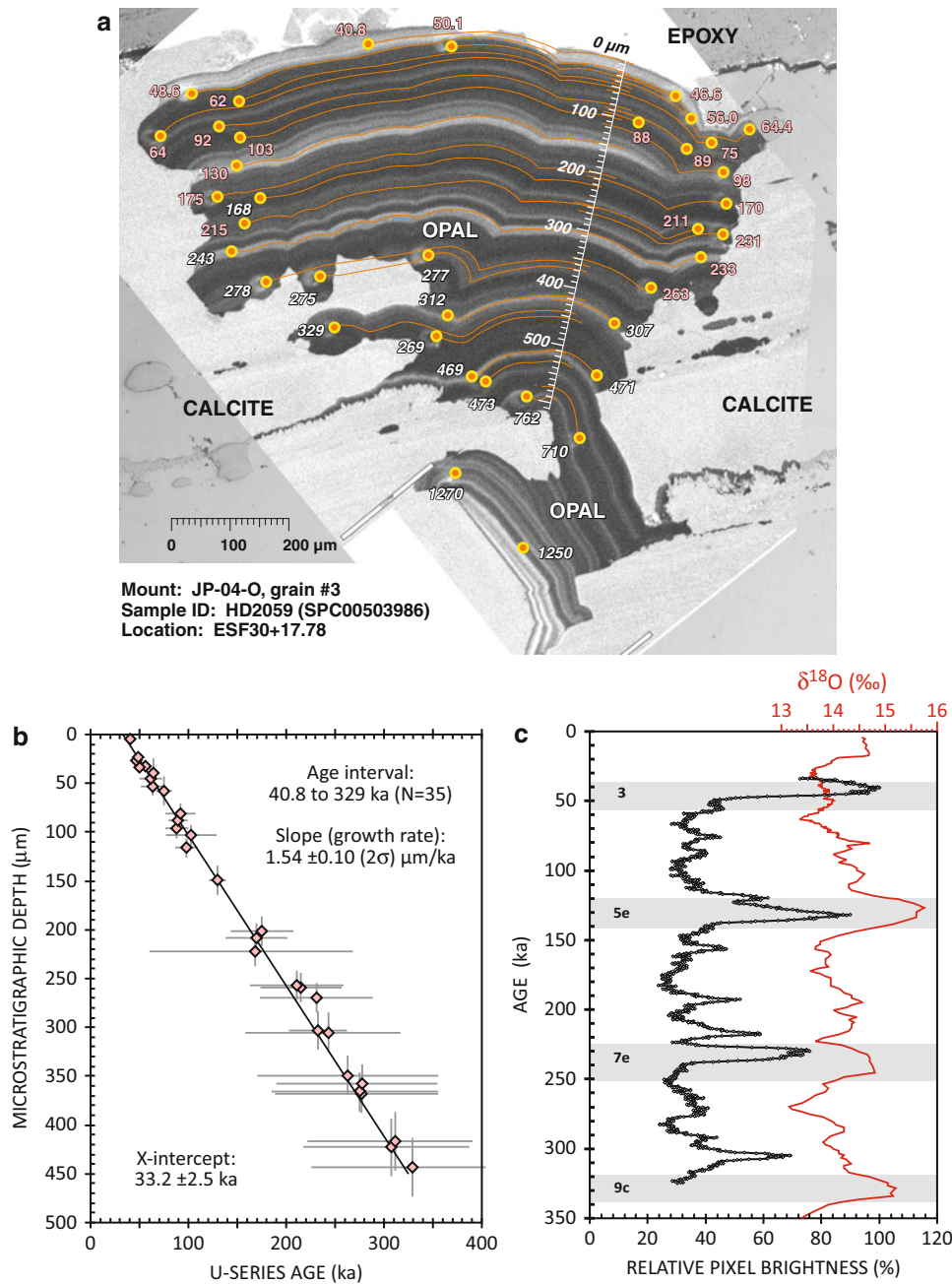


Fig. 3 U-series dating results for a sample of hyalitic opal from the deep vadose zone at Yucca Mountain, Nevada. **(a)** Cathodoluminescence (CL) image of growth-zoned opal showing locations of secondary ion mass spectrometry spot analyses and calculated ages (all given in ka, with $^{230}\text{Th}/\text{U}$ ages shown in pink and model $^{234}\text{U}/^{238}\text{U}$ ages shown in italics). **(b)** Relation between depth and age for points shown in **(a)**. Slope of linear regression represents the long-term average opal growth rate. **(c)** Age-adjusted profile of relative pixel brightness for the outermost ~500 μm of the CL image shown in **(a)**. The calcite $\delta^{18}\text{O}$ profile from the Devils Hole climate record is shown in red for comparison along with gray bands representing interglacial or interstadial episodes for marine isotope stages 3, 5e, 7e, and 9c (Modified after Figs. 2, 4, and 7 of Paces et al. (2010), and Fig. 5 of Winograd et al. (2006))

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Carbonates, Speleothem Climatic, \(U-Series\)](#)
- ▶ [Cements, Pedogenic \(U-Series\)](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Secondary Ion Mass Spectrometer \(SIMS\)](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [Uranium-Lead Dating, Opal](#)
- ▶ [U-Series Dating](#)

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Uranium Series, Volcanic Rocks

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Synonyms

$^{226}\text{Ra}/^{230}\text{Th}$ dating; $^{230}\text{Th}/\text{U}$ dating; Uranium-series isotope disequilibrium; U-series geochronology

Definitions

SIMS: Secondary ion mass spectrometry (SIMS) is a high spatial resolution technique that uses a focused beam of ions (primary beam) to bombard a sample surface and generate secondary ions that are accelerated into a mass spectrometer for measurement of isotopic abundances.

Magmatic differentiation: Physicochemical events, such as fractional crystallization, that modify the chemical composition of magmas.

Phenocryst: Relatively large crystal present in a finer grained crystalline or glassy groundmass.

Autocryst: A crystal that is spatially and temporally associated with a distinct pulse or increment of magma.

Antecryst: A crystal from an earlier pulse of magma which is incorporated by later pulses.

Xenocryst: A crystal incorporated from host rocks during transit and emplacement of magmas.

Introduction

Application of U-series dating to volcanic rocks provides unique and valuable information about the absolute timing of crystallization and differentiation of magmas prior to eruption. The ^{238}U – ^{230}Th and ^{230}Th – ^{226}Ra methods are the most commonly employed for dating the crystallization of mafic to silicic magmas that erupt at volcanoes. Dates derived from the U–Th and Ra–Th methods reflect crystallization because diffusion of these elements at magmatic temperatures is sluggish (Cherniak 2010) and diffusive re-equilibration is insignificant over the timescales ($\leq 10^5$ years) typically associated with pre-eruptive storage of nearly all magma compositions (Cooper and Reid 2008). Other dating methods based on elements that diffuse rapidly at magmatic temperatures, such as the $^{40}\text{Ar}/^{39}\text{Ar}$ and (U–Th)/He methods, yield dates for the cooling of magma at the time of eruption. Disequilibrium of some short-lived daughters of the uranium series such as ^{210}Po may be fractionated by saturation of a volatile phase and can be employed to date magmatic gas loss that is synchronous with volcanic eruption (e.g., Rubin et al. 1994).

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Dating Volcanic Rocks Using U-Series Isochrons and Model Ages

Isochrons and model ages are most commonly employed for U-series disequilibrium dating of volcanic rocks. As in other methods, the use of U-series isochrons assumes that component minerals or a set of rocks are cogenetic, are coeval, share the same initial daughter activity, e.g., $(^{230}\text{Th})/(^{232}\text{Th})$, and isotopically evolve within a closed system. The U-series isochrons used for dating volcanic rocks are representations of parent-daughter nuclide evolution as a function of time:

$$(N_1) = (N_2)(1 - e^{-\lambda_1 t}) + (N_1)_0 e^{(-\lambda_1 t)},$$

where (N_1) is the daughter activity, (N_2) is parent nuclide activity, $(N_1)_0$ is initial daughter nuclide activity, λ_1 is decay constant of the daughter, and t is time. Parent and daughter nuclide activities are typically normalized to the activity concentration of a stable or relatively long-lived isotope of the daughter nuclide, e.g., ^{232}Th in the case of ^{238}U – ^{230}Th dating. Minerals or rocks satisfying the aforementioned assumptions form isochrons (Fig. 1) with an age-proportional slope = $(1 - e^{-\lambda_1 t})$. When parent and daughter reach secular equilibrium, the isochron slope is equal to unity (i.e., $(^{230}\text{Th})/(^{238}\text{U}) = 1$).

For volcanic rocks, U-series isochrons are typically constructed from phenocryst and melt (glass or crystalline groundmass) phases or geochemically variable suites of volcanic rocks. Model ages may be derived for single whole rocks or minerals by assuming the initial magnitude of parent-daughter disequilibrium. For example, U and Th are fractionated between crystals and their parent melt according to the crystal-melt partition coefficients for individual phases, resulting in variable deficits or excesses of ^{238}U or ^{230}Th (as well as the other shorter-lived daughters) in crystals and associated melt (i.e., a range of $(^{238}\text{U})/(^{232}\text{Th})$ values in Fig. 1). High-temperature crystallization does not result in measurable $^{238}\text{U}/^{234}\text{U}$ or $^{230}\text{Th}/^{232}\text{Th}$ fractionation. Hence, the activity of ^{230}Th can be directly compared to that of grandparent ^{238}U , and coeval minerals and melts will share the

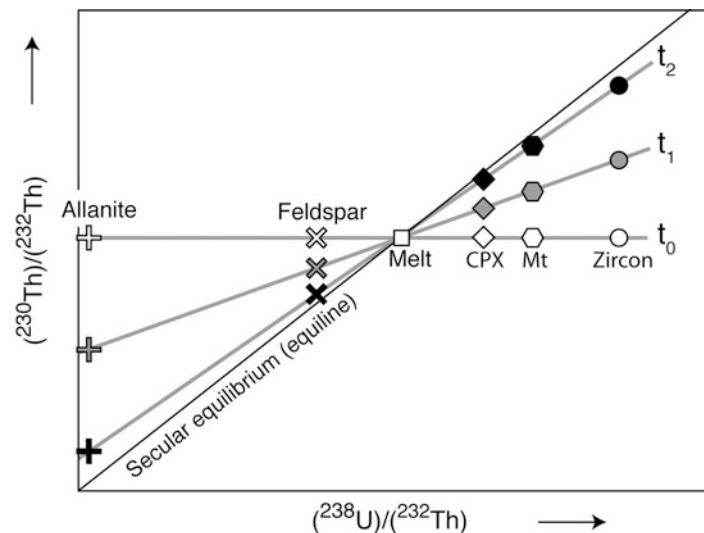


Fig. 1 Schematic ^{238}U – ^{230}Th isochron for a single volcanic rock containing multiple phases (allanite, feldspar, melt, clinopyroxene [CPX], magnetite [Mt], and zircon) with variable U/Th. Gray lines link the isochronous phases at the time of crystallization (t_0) and subsequent periods of time (t_1 , t_2) as a consequence of ingrowth or decay of ^{230}Th . If crystallization at t_0 occurs shortly before eruption, the isochron effectively dates volcanism. If crystallization is protracted relative to ^{230}Th evolution, then the isochron predates volcanism

same initial $^{230}\text{Th}/^{232}\text{Th}$. However, fractionation of uranium isotopes can take place in lower-temperature aqueous environments, and volcanic rocks with measured $(^{234}\text{U})/(^{238}\text{U}) \neq 1.0$ indicate the presence of secondary alteration and/or recycling of crystals from older altered rocks.

After ~ 5 daughter half-lives, parent and daughter nuclides effectively reach secular equilibrium. In the case of ^{238}U – ^{230}Th , secular equilibrium occurs after ~ 350 ka, while in the case of ^{230}Th – ^{226}Ra , after ~ 8 ka. Accordingly, the U–Th and Th–Ra methods can potentially date crystallization with a resolution of hundreds to thousands of years. Th–Ra isochrons for volcanic rocks are complicated because Ra lacks a stable nuclide for parent-daughter normalization. Ba may be used as an imperfect analogue to Ra, but significant subequal Ra/Ba fractionation between minerals results in isochrons with kinked typology (Cooper et al. 2001). Consequently, theoretical or experimental limits on Ra/Ba partitioning are required to determine the initial $^{226}\text{Ra}/[\text{Ba}]$ of each mineral at the time of crystallization (Cooper and Reid 2008).

An internal isochron constructed from multiple minerals provides a crystallization date for the magma represented by that individual volcanic rock. An external isochron constructed from a suite of cogenetic volcanic rocks provides a date for the fractional crystallization responsible for the suite of related magmas. In each case, instantaneous crystallization or fractionation is assumed. As with other isochron methods, dating precision is maximized when minerals or rocks exhibit a large contrast in parent/daughter ratios. For example, isochrons pairing accessory minerals such as zircon and allanite, whose U/Th ratios vary by orders of magnitude, may yield late Pleistocene ages with $<5\%$ precision (Simon et al. 2009). To date volcanic eruptions, the crystallization or fractionation responsible for U-series isochrons must occur shortly before eruption. Examples are the coherent isochrons generated from major phases including feldspar, glass, pyroxene, and magnetite from late Pleistocene-Holocene andesitic and rhyolitic lavas at Puyehue-Cordon Caulle, Chile, and Segum Island, Alaska, USA, which yield ^{238}U – ^{230}Th ages that are indistinguishable from their associated $^{40}\text{Ar}/^{39}\text{Ar}$ eruption ages (Jicha et al. 2005, 2007).

Model ages may be calculated for individual volcanic rocks or minerals by assuming that $(^{230}\text{Th})/(^{238}\text{U})$ or $^{226}\text{Ra}/[\text{Ba}]$ is controlled by the initial magnitude of disequilibrium and the time elapsed since eruption. Limits on the initial magnitude of disequilibrium can be inferred from related samples that are effectively zero age. This approach is especially useful for volcanic rocks that lack substantial Th–U or Ra–Th variation and/or have few phenocrysts. For example, observed limits on the initial $(^{230}\text{Th})/(^{238}\text{U})$ and $(^{226}\text{Ra})/(^{230}\text{Th})$ values for mid-ocean ridge basalt (MORB) erupted from segments of the East Pacific Rise allow calculation of model ages for eruption, which in turn, yields spreading rates and recognition of youthful, off-axis volcanism (Rubin and Macdougall 1990; Zou et al. 2002). A similar approach using ^{210}Pb – ^{210}Po disequilibrium has been used to date MORB lavas younger than 2 years (Rubin et al. 1994).

Complexities in Dating Volcanic Rocks

Dating volcanic rocks by U-series disequilibrium is complicated when pre-eruption crystallization is protracted and/or recycling of “old” crystals is significant. Precise analyses of major phases using thermal or plasma ionization mass spectrometry require up to several grams of bulk material that may combine hundreds to thousands of crystals, and yield concentration-weighted mean ages integrating the entire crystallization interval (Cooper and Reid 2008). Accordingly, the presence of antecrysts and/or xenocrysts causes U-series dates to be skewed toward values older than eruption.

Scattered arrays of data on a mineral-isochron diagram imply crystal recycling or the mixing of magmas with different crystal populations (e.g., Pyle et al. 1988). Isochrons derived from analyses of multiple mineral and/or glass separates that exhibit little scatter suggest coherent age populations that are minimally skewed by recycled crystals (e.g., Jicha et al. 2005, 2007). Analyses of groundmass crystals or glass are likely to represent near-eruption crystallization and are targets for U-series dating of volcanic rocks (e.g., Bourdon et al. 1994). Small-volume basalts are unlikely to have significant residence in the crust, so their isochrons determined from phenocrysts and groundmass crystals are likely to effectively date eruption. For example, the ^{238}U – ^{230}Th isochron age for mafic lava recording the Laschamp geomagnetic excursion is indistinguishable from the ca. 41 ka derived from independent dating methods such as $^{40}\text{Ar}/^{39}\text{Ar}$ and layer counting of Greenland ice cores (Singer et al. 2009). Dates derived from isochron or model-age methods using whole-rock samples may be complicated by magma mixing where resulting isotopic compositions represent pseudo-isochrons or “errorchrons” that are in fact mixing lines between the two end members.

Resolving Near-Eruption Ages Using High Spatial Resolution Dating of Accessory Minerals

Individual accessory minerals with enriched concentrations of U and Th, such as zircon and allanite, are datable using the in situ sampling capability of ion microprobe analysis by secondary ion mass spectrometry (SIMS). Although analyses are not as precise as those determined using thermal or plasma ionization mass spectrometry, SIMS U–Th dating can reveal 10^3 – 10^5 -year age variations within single crystals, which allows crystal-by-crystal discrimination between autocrysts, antecrysts, and xenocrysts (Cooper and Reid 2008; Schmitt 2011). The final increment of crystallization preserved by U- and Th-rich minerals can be dated via SIMS analysis of unpolished faces on single crystals embedded in soft metal (Fig. 2). This approach samples the outermost few micrometers on single crystals and is superior in spatial resolution to the traditional SIMS approach of

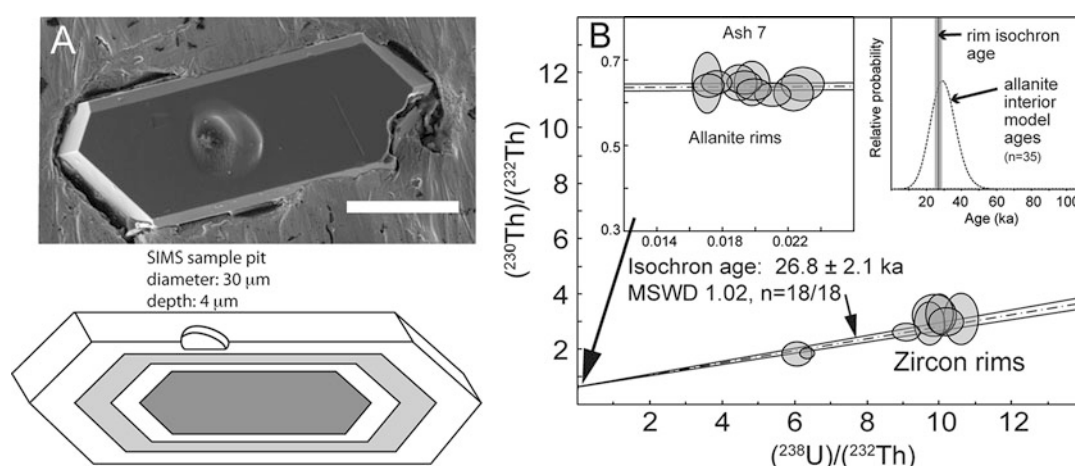


Fig. 2 (a) Secondary electron image of SIMS analysis pit on the face of an unpolished euhedral zircon. White bar is 50 μm . Cartoon illustrates how the several micrometer depth resolutions of the SIMS primary beam are used to sample the final increment of zircon crystallization. (b) Late Pleistocene isochron from SIMS analyses of crystal faces on zircon and allanite from a rhyolitic tephra in California. Model ages for the interiors of the allanite are calculated assuming the same initial $(^{230}\text{Th})/(^{232}\text{Th})$ as the rims. The ca. 27 ka rim isochron age matches the tephra age from magnetostatigraphy (Modified from Vazquez and Lidzbarski 2012)

dating cross-sectioned crystals (Fig. 2). The euhedral faces of coexisting crystals are likely to be time equivalent and cogenetic and hence can yield isochron dates for near-eruption crystallization. Isochrons constructed using data from the rims of coexisting zircon and allanite in rhyolitic tephras from Mono Craters, east-central California (Fig. 2), yielded crystallization ages that agree with independent dating by magnetostratigraphy and the (U–Th)/He method (Vazquez and Lidzbarski 2012).

Summary

Volcanic rocks can be dated using several pairs of parent-daughter isotopes in the U-series decay chain. Dates ranging from several thousands to several hundreds of thousands of years are commonly obtained using isochron methods determined on multiple mineral phases within a single rock or analyses of multiple rock samples in a cogenetic suite. Model ages may also be calculated if reasonable assumptions about initial disequilibrium can be made. Resulting dates can reflect either eruptive ages or more convoluted stages of magma evolution depending on the nature of the crystallization processes that took place and the types of analyses that were conducted.

Cross-References

- ▶ [Ar–Ar and K–Ar Dating](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Secondary Ionization Mass Spectrometry \(SIMS\)](#)
- ▶ [Thermal Ionization Mass Spectrometry \(TIMS\)](#)
- ▶ [Uranium Series, Rates of Basaltic Melt Generation and Transport](#)
- ▶ [U-Series Dating](#)
- ▶ [U–Th:He Dating](#)
- ▶ [Zircon](#)

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Neutron Activation Analysis

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Definition

Neutron activation analysis is a chemical analysis technique that may be used to determine the average (bulk) concentrations of major, minor, and trace elements in a sample. It may be used to measure the concentration of a single element or, more often, to measure the concentrations of many elements, as part of a chemical characterization of a set of samples to determine chemical similarities or differences. Samples may be liquid (aqueous or organic) or solid (e.g., animal tissues, ceramics, clays, glasses, paper, plants, plastics, lithics, metals).

The most common form of neutron activation analysis is instrumental neutron activation analysis. In this, a suitably encapsulated, weighed amount of the sample to be analyzed is sent, pneumatically or manually, into an irradiation site of a research nuclear reactor, and is bombarded by neutrons with a broad range of energies that the reactor produces.

Once the sample has been irradiated for an appropriate time, it is removed from the irradiation site and the induced radioactivity measured by counting the sample using a gamma-ray spectrometer. The result of counting produces a gamma-ray spectrum in which specific gamma-ray energies produce peaks, the areas of which are proportional to the amount of the element that is responsible for the gamma-rays.

To determine the actual amount of an element in a sample, peak areas are compared with calibrations taken from a stored library of information or from a similarly run substandard of the element.

There are three types of neutron activation reactions: (n, γ) , a neutron is absorbed by an atomic nucleus and a gamma-ray is emitted; (n, p) , a neutron is absorbed by an atomic nucleus and a proton is emitted; and (n, α) , a neutron absorbed by an atomic nucleus and an alpha particle is emitted. The first nuclear reaction is generated by low-energy (<0.1 eV or thermal) neutrons, and the other two are produced mainly by epithermal and fast (>1 MeV) neutrons. Although thermal neutron reactions are favored highly, some activation products may arise from elements of different atomic numbers. For example, ^{28}Al is produced preferentially by the thermal neutron reaction $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$, by the epithermal neutron reaction $^{28}\text{Si}(n, p)^{28}\text{Al}$, and by the fast neutron reaction $^{31}\text{P}(n, \alpha)^{28}\text{Al}$. This means that while it is potentially impossible to analyze for Si, P, and Al in a matrix including large amounts of each, it is possible to use the activation product ^{28}Al to analyze for Al in alumina-silicate materials; for Si in silica-rich, or doped, materials; and for P in bones.

Only a minute fraction of the neutrons that hit a sample actually interact with nuclei of atoms in the sample to form artificial radioactivity. Elements form radioisotopes that emit one or more gamma-rays with discrete energies and that decay with characteristic half-lives, labeled short, medium, or long. For an analysis, knowledge of expected half-lives helps determine the irradiation time, the delay time before counting, and the counting time.

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A more detailed view of the principles of neutron activation analysis (NAA) can be found in Kruger (1971), Neff (2000), or Pollard and Heron (1996).

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Uranium-Lead, Rubidium-Strontium, Kimberlite

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Introduction

Kimberlites are small-volume, highly gas-charged magmas derived from great depths in the mantle that, due to their explosive nature and fast ascent rates, have a great carrying capacity to entrain and transport material from the mantle to the Earth's surface. Some of the entrained material includes fragments of mantle rock (peridotite, eclogite, pyroxenite), which are invaluable for directly studying the nature of the deep Earth, and rare minerals that only form at great depth (e.g., diamond, majorite garnet). They are also the source of primary diamond deposits at the Earth's surface.

Determining the composition and emplacement age of kimberlites has long been a challenge because kimberlites are heterogeneous rocks consisting of a mixture of primary minerals that crystallize directly from the kimberlite magma and both mantle and crustal material that have been entrained during magma ascent. Figure 1a is a whole rock sample from the Monastery kimberlite illustrating the heterogeneous nature with mantle xenoliths (MX), crustal xenoliths (CX), and ilmenite megacrysts (ilm). In addition to the relative emplacement age constraint imposed by cross-cutting relationships with crust of known formation age, there have been several absolute radiometric dating methods applied to whole rock kimberlite samples and constituent minerals with varying degrees of success (e.g., Allsopp and Roddick 1984; Basu et al. 1984; Allsopp et al. 1986; Blackburn et al. 2008; Noyes et al. 2011), including K-Ar (whole rock, phlogopite), $^{40}\text{Ar}/^{39}\text{Ar}$ (phlogopite, clinopyroxene), fission track (zircon, apatite), U-Pb (zircon, perovskite, ilmenite, rutile), U-Th/He (apatite, zircon, titanite, magnetite, garnet), and Rb-Sr (phlogopite). In this contribution the methodology and limitations of two commonly used radiometric dating techniques for determining the emplacement age of kimberlites, U-Pb and Rb-Sr, will be reviewed.

U-Pb Geochronology of Kimberlite Minerals

The U-Pb technique is based on the radioactive decay of two long-lived uranium isotopes, ^{238}U and ^{235}U , to two different radiogenic lead isotopes, ^{206}Pb and ^{207}Pb , respectively, with decay constants of $1.55125 \times 10^{-10} \text{ year}^{-1}$ (half-life of 4.47 Ga) and $9.8485 \times 10^{-10} \text{ year}^{-1}$ (half-life of 0.704 Ga). This technique is unique compared to other geochronology methods in that each measurement derives an age from two distinct U-Pb clocks (Jaffey et al. 1971). For most U-Pb age determinations, a measure of the internal consistency of the age is the degree to which these two U-Pb clocks are in agreement, also known as the degree of concordancy, thereby making it possible to test if the system has been disturbed by post-crystallization processes. The ideal U-Pb chronometer is a mineral or whole rock that contains only uranium and no lead at the time of formation; some

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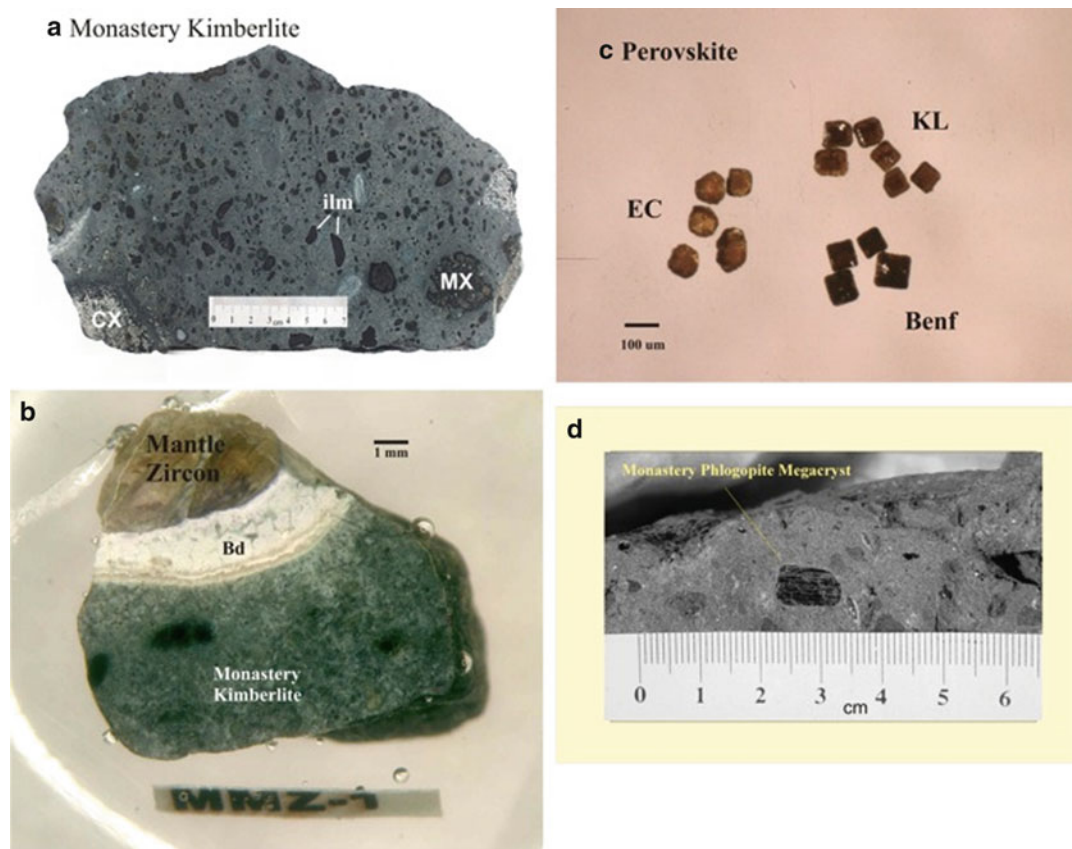


Fig. 1 Examples of materials used for U-Pb and Rb-Sr dating of kimberlites. (a) Whole rock kimberlite illustrating a heterogeneous texture with mantle xenoliths (MX), crustal xenoliths (CX), and megacryst minerals such as ilmenite (ilm). (b) Mantle zircon megacryst hosted in Monastery kimberlite: note the white reaction rim that consists dominantly of baddeleyite (Bd). (c) Examples of isolated groundmass perovskite from three different kimberlites: *EC* Elliott County, *KL* Kirkland Lake, and *Benf* Benfontein sill. (d) Phlogopite megacryst in Monastery kimberlite used for Rb-Sr dating

minerals approach this condition, such as zircon, baddeleyite, and monazite. The abundance of lead in a mineral at the time of crystallization is referred to as initial common lead, and the amount can be determined by measuring the abundance of ^{204}Pb , an isotope of lead that is not produced by radioactive decay.

For relatively young samples (e.g., Phanerozoic), the ^{238}U - ^{206}Pb chronometer is the most commonly used because the abundance of radiogenic ^{206}Pb is substantially higher than ^{207}Pb , due to a combination of the different decay rates of the two U parent isotopes and the two orders of magnitude difference in their abundance ($^{238}\text{U}/^{235}\text{U} = 137.82$, Hiess et al. 2010; revised slightly from 137.88, Jaffey et al. 1971). For these reasons, the ^{238}U - ^{206}Pb chronometer is least sensitive to any common Pb correction, so assuming there is no disturbance to the system (e.g., Pb-loss), this is the most commonly used method applied to kimberlite minerals and mantle materials. An excellent overview of the U-Pb dating technique has been recently published by Blair Schoene (2014).

There are a number of analytical techniques that have been used to determine U-Pb dates of kimberlites including isotope dilution thermal ionization mass spectrometry (IDTIMS; e.g., Heaman 1989; Smith et al. 1989; Heaman and Kjarsgaard 2000), laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS; e.g., Cox and Wilton 2006; Simonetti et al. 2008; Batumike et al. 2008; Yang et al. 2009; Wu et al. 2010), and secondary ion mass spectrometry

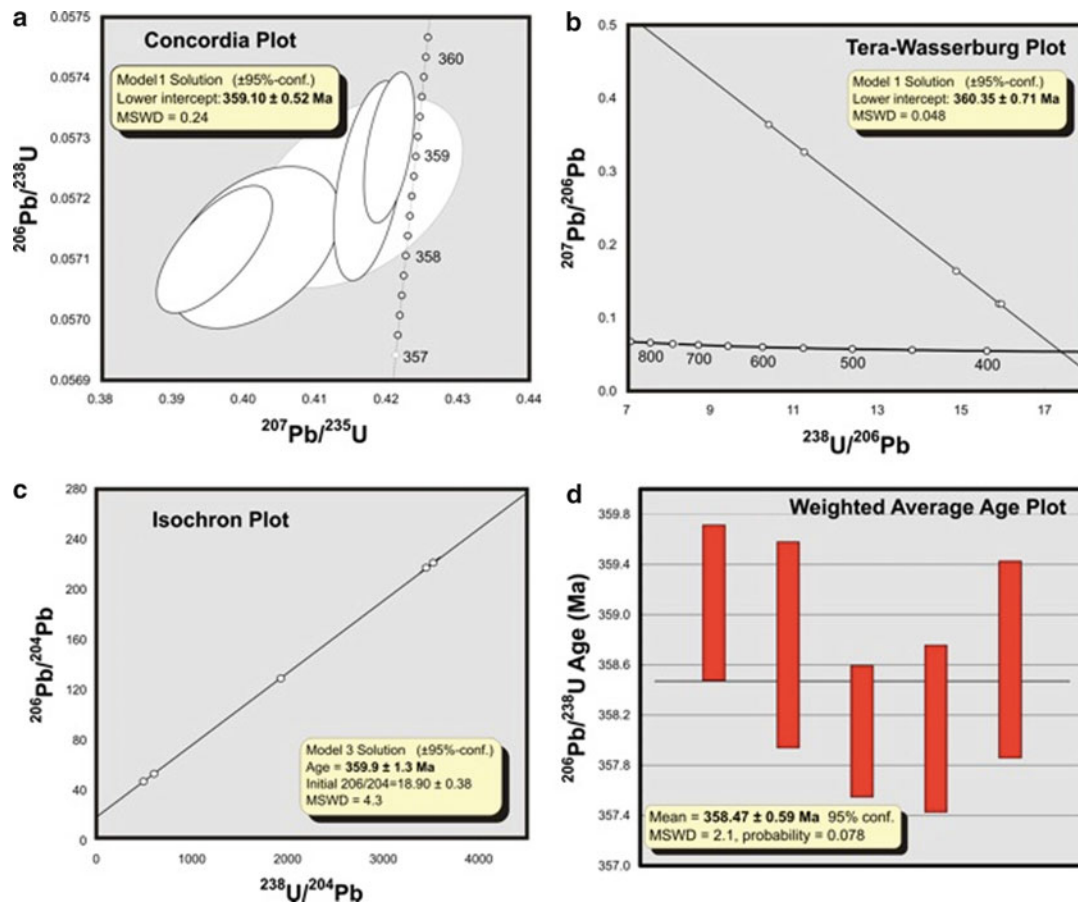


Fig. 2 Examples of four different methods to represent U-Pb results using five aliquots of perovskite from a single crystal: (a) concordia plot, (b) Tera-Wasserburg plot, (c) isochron plot, and (d) weighted average $^{206}\text{Pb}/^{238}\text{U}$ age

(SIMS; e.g., Kinny et al. 1997; Li et al. 2010; Chalapathi Rao et al. 2013; Wu et al. 2013). For IDTIMS analyses the sample material is dissolved in acids, U and Pb purified using anion exchange chromatography, and their isotopic compositions determined using a thermal ionization mass spectrometer (Heaman 1989). Ion beam dating techniques can be applied to isolated crystals secured in an epoxy mount or in situ by directly dating crystals in a petrographic thin section. The U-Pb results can be presented on a variety of plots including concordia ($^{207}\text{Pb}/^{235}\text{U}$ vs. $^{206}\text{Pb}/^{238}\text{U}$; Fig. 2a), Tera-Wasserburg ($^{238}\text{U}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$; Fig. 2b), isochron ($^{238}\text{U}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; Fig. 2c), and weighted average $^{206}\text{Pb}/^{238}\text{U}$ age (Fig. 2d) diagrams. In most cases the method of calculating the dates does not affect the resulting ages as long as the amount of common lead is accurately known. For example, perovskite dates have been calculated for five aliquots of the same crystal by the various methods graphically portrayed in Fig. 2 resulting in ages that vary between 358.5 and 360.4 Ma but they all overlap within analytical uncertainty.

U-Pb Mantle Zircon

The occurrence of zircon (ZrSiO_4) in kimberlite has been known for a long time (Ahrens et al. 1967; Kresten et al. 1975), but the application of U-Pb mantle zircon dating to constrain the emplacement age of kimberlites can be attributed to the pioneering research of Gordon Davis and

colleagues at the Carnegie Institute of Washington in the 1970s (e.g., Davis et al. 1976; Davis 1977, 1978). Mantle zircon occurs as a sparse but relatively large (cm-size crystals) accessory mineral in kimberlites (Fig. 1b) and has been documented at a few kimberlite localities (Kresten et al. 1975). Figure 1b is a mantle zircon hosted within the Monastery kimberlite with a 1–2 mm wide reaction rim consisting dominantly of baddeleyite (white). Mantle zircons are commonly recovered during bulk sampling and final processing as a by-product of diamond mining due to its high density (4.7 g/cm^3) and fluorescence properties. Mantle zircon can occur as isolated rounded megacrysts of variable color but commonly honey-colored (Kresten et al. 1975), as inclusions in diamond (Kinny and Meyer 1994), or as an accessory mineral in mantle material entrained in kimberlite (Davis et al. 1976; Kinny and Dawson 1992; Chen et al. 1994; Hamilton et al. 1998; Konzett et al. 1998; Heaman et al. 2002). A very diagnostic feature of mantle zircon is the formation of baddeleyite-dominated reaction rims (white rim in Fig. 1b) that result from desilicification once entrained in kimberlite magma (Kresten et al. 1975; Heaman and LeCheminant 1992). The presence of these baddeleyite rims, large crystal size (mm to cm), and unusual chemical composition such as their typically low U and Th (<10 ppm) and Y (<100 ppm) concentrations (Heaman et al. 1990; Belousova et al. 1998; 2002) helps to distinguish mantle zircon from the more common crustal zircon xenocrysts in kimberlite.

The origin of zircon megacrysts in kimberlite is uncertain, but they form part of a megacryst suite that have been interpreted as high-pressure phenocrysts that crystallized directly in the kimberlite magma or more likely as mantle xenocrysts that originally formed as part of a magma cumulate or metasomatic veins in the mantle (Moore et al. 1992). Depending on their origin in the subcontinental mantle, they may belong to geological events that precede kimberlite magmatism. The common interpretation that mantle zircon U-Pb dates record the time of kimberlite eruption is based on the fact that these crystals reside in the lithospheric mantle at temperatures that exceed the closure temperature for Pb diffusion ($>900^\circ\text{C}$; Lee et al. 1997) and only begin to accumulate radiogenic lead once they are transported by the rapid ascent of kimberlite magma to lower temperature regions in the crust. It is likely that this assumption is valid in most cases (exceptions are noted below) and has guided the application of U-Pb mantle zircon geochronology to obtain ages of kimberlite emplacement. Although there are few well-studied examples that prove U-Pb mantle zircon megacryst dates record the timing of kimberlite emplacement, a detailed study using a variety of radiometric dating methods (U-Pb zircon, U-Pb perovskite, Rb-Sr phlogopite) applied to minerals contained in the Monastery kimberlite (Noyes et al. 2011) demonstrates excellent internal agreement between dates obtained on megacrysts and groundmass crystals, confirming the assumption that mantle zircon megacrysts can be used to accurately date the time of kimberlite emplacement.

However, there are a handful of examples where mantle zircon dates record pre-kimberlite eruption age information. Kinny et al. (1989) documented two age populations of mantle zircon in the Jwaneng DK2 kimberlite: a Permian population similar to the emplacement age of the kimberlite and a much older disturbed Archean population. In addition, Kinny and Meyer (1994) report a concordant 628 Ma U-Pb SHRIMP age for a zircon inclusion in diamond from the Cretaceous Mbuji Mayi kimberlite, Zaire, further evidence that mantle zircon can preserve its original formation age, at least when encapsulated in diamond. Other examples of U-Pb zircon pre-kimberlite emplacement ages have been documented from zircon contained in mantle xenoliths (Konzett et al. 1998; Hamilton et al. 1998; Heaman et al. 2002). In summary, there is unequivocal evidence that certain mantle zircons can preserve pre-kimberlite age information and are not always completely reset under high-pressure and high-temperature conditions of the subcontinental mantle, so some caution is required in interpreting U-Pb mantle zircon dates.

U-Pb Groundmass Perovskite

Perovskite (CaTiO_3) is a common accessory mineral in many kimberlites (abundance is typically <1 vol.% of the rock) and typically forms tiny (<100 μm), euhedral-subhedral, orange-brown cubes/octahedra. Figure 1c shows three examples of isolated perovskite crystals from kimberlite: EC, Elliott County, Kentucky; KL, Kirkland Lake, Quebec; and Benf, Benfontein sill, S. Africa. Perovskite paragenesis in kimberlite can be variable (Chakhmouradian and Mitchell 2000; Mitchell 2002), most commonly as isolated crystals in the groundmass and to a lesser extent as inclusions in other minerals, such as phlogopite and occasionally diamond (Hamilton et al. 2003; Bulanova et al. 2010); as reaction-induced rims on earlier formed Ti-minerals (e.g., ilmenite); as a cumulate mineral in sill-like bodies (e.g., Benfontein sill); as polycrystalline glomerocrysts; or as a string of crystals (necklace texture) nucleating on earlier formed phenocrysts/megacrysts (e.g., olivine, phlogopite, or spinel).

Kimberlitic perovskite typically forms stoichiometrically near end-member CaTiO_3 (Chakhmouradian and Mitchell 2000; Mitchell 2002) and contains elevated levels of several minor elements, including Fe, Na, Sr, Nb, Ta, and Th, and the light rare earth elements. The moderate amounts of Sr (500–4,000 ppm), Nd (1,000–10,000 ppm), and to a lesser extent Hf (50–200 ppm) in perovskite make it an ideal petrogenetic tracer; the isotopic composition of these elements has been used in a few studies to trace the mantle origin and evolution of kimberlite magmas (e.g., Heaman 1989; Paton et al. 2007; Yang et al. 2009; Malarkey et al. 2010; Zurevinski et al. 2011). Based on a fission track study of kimberlite minerals, Kleeman and Lovering (1973) showed that kimberlitic perovskite is enriched in uranium compared to other minerals in the groundmass, such as calcite.

U-Pb dating of perovskite is a preferred choice for dating kimberlite emplacement because in most cases it crystallizes directly from the kimberlite magma. Perovskite occurs in many kimberlites and related rocks (aillikite, carbonatite, lamproite, ultramafic lamprophyre), but very little is known about what controls perovskite crystallization in these magmas. Primary magmatic perovskite is most common in hypabyssal kimberlite and to a lesser extent in diatreme or crater facies kimberlite. Perovskite xenocrysts have been reported (Heaman 1989) but are rare because, unlike in the case of zircon, most crustal rocks do not contain perovskite. Based on more than 1,000 perovskite analyses, the range of U and Th/U in the majority of pure kimberlitic perovskite aliquots varies between 20–200 ppm and 1–40 ppm, respectively. Perovskite analyses with very high U (up to 1,500 ppm; Wu et al. 2013) or Th/U (up to 200; Heaman and Kjarsgaard 2000) have been reported but are considered outliers and may reflect the presence of high U and/or Th mineral inclusions (such as uraninite or thorite). The contents of U and Th are much higher in kimberlitic perovskite than meteoritic perovskite (Ireland et al. 1990) or diamond inclusion perovskite (Bulanova et al. 2010), which typically contain <10 ppm of these elements and can have $\text{Th}/\text{U} < 1$.

U-Pb dating of perovskite was pioneered in the 1980s (Kramers and Smith 1983; Smith et al. 1989; Heaman 1989) and since that time there have been more than 1,000 U-Pb perovskite dates reported for kimberlites utilizing all the U-Pb dating techniques (e.g., Heaman 1989; Smith et al. 1989; Kinny et al. 1997; Batumike et al. 2008; Yang et al. 2009; Li et al. 2010). There are three main challenges in dating perovskite: (1) the small grain size (often <50 μm), making it difficult to extract from the whole rock using conventional mineral separation techniques and difficult to analyze by ion beam U-Pb techniques (e.g., LA-ICPMS requires a 30–40 μm diameter spot for a precise analysis); (2) it contains a significant amount of common Pb (10–30 % of the total Pb), so any age calculation is sensitive to the common Pb correction; and (3) it can be easy to confuse with

other minerals (e.g., spinel, slightly tarnished sulfide) in a concentrate using a binocular microscope at the highest magnification. Some caution is necessary for kimberlitic “perovskite” analyses that contain low uranium contents (<20 ppm) and low Th/U (<1) because they likely represent mixtures of perovskite combined with one or more contaminants (this is not a problem for in situ techniques).

The amount of perovskite required for a precise analysis has dramatically decreased over the past 20 years and accurate U-Pb IDTIMS dates can be obtained on 10–20 µg aliquots (~1–100 crystals depending on grain size), and crystals as small as 15 µm in diameter have been successfully isolated from kimberlite whole rock and dated using this technique. Most of the in situ U-Pb perovskite dating studies of kimberlites have used either the LA-ICPMS (Batumike et al. 2008; Yang et al. 2009; Wu et al. 2010) or SIMS (Smith et al. 1994; Kinny et al. 1997; Li et al. 2010; Chalapathi Rao et al. 2013; Wu et al. 2013) techniques with analysis spot diameters typically on the order of 40 and 25 µm, respectively. Cox and Wilton (2006) report smaller diameter analysis spots (down to 10 µm) for U-Pb LA-ICPMS perovskite dates from the Oka carbonatite. The precision and accuracy of perovskite dating is limited by the uncertainty in the common Pb correction (not all studies propagate the uncertainty in the common Pb composition in the resulting age uncertainties). Most often the initial common Pb composition of perovskite is calculated from the two-stage crustal Pb evolution model of Stacey and Kramers (1975). Although it is unclear that this model is appropriate for kimberlites, it does approximate the Pb isotopic compositions of Group 1 whole rock kimberlite (Smith 1983). For a Jurassic perovskite containing 20 % total common Pb, the effect on a U-Pb perovskite age calculation using an average crustal Pb versus an average depleted mantle Pb is ~5 m.y. An alternative approach is to use a low $^{238}\text{U}/^{204}\text{Pb}$ primary mineral (e.g., titanomagnetite) that crystallizes directly from the kimberlite magma to constrain the initial Pb isotopic composition. For example, Burgess et al. (2012) showed that using an Earthtime calibrated tracer solution resulted in a more precise weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 357.17 ± 0.27 Ma compared to the previously reported date of 356.5 ± 1.0 Ma (Heaman 2009) for fragments from the same Ice River perovskite crystal and that the accuracy of the date could be improved by using clinopyroxene ($^{238}\text{U}/^{204}\text{Pb} < 500$) to derive a more accurate estimate of the initial Pb isotopic composition.

U-Pb Dating: Other Minerals

Although groundmass perovskite and mantle zircon are the most common minerals used in dating kimberlites by the U-Pb method, there have been attempts to utilize other less common U-bearing minerals, such as baddeleyite (ZrO_2 ; Schärer et al. 1997; Heaman and LeCheminant 2000; Li et al. 2011), ilmenite (FeTiO_3 ; Noyes et al. 2011), and rutile (TiO_2 ; Cooper et al. 2008). There has been some success using other U-bearing minerals to date kimberlite emplacement but there is always a challenge to prove that the dates obtained reflect the time of kimberlite emplacement and not the age of mantle or crustal xenocrysts, potentially recording dates that significantly predate kimberlite eruption.

Rb-Sr Phlogopite Geochronology

The Rb-Sr dating technique is based on the beta decay of radioactive parent ^{87}Rb with a decay constant of $1.42 \times 10^{-11} \text{ year}^{-1}$ (Davis et al. 1977; half-life of 48.8 Ga) to daughter ^{87}Sr . The

geochemical behavior of Rb follows closely that of potassium because they are both monovalent and have similar ionic radii, so K-rich minerals, such as phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$), are ideal for Rb-Sr geochronology because there is significant Rb but negligible common Sr substitution in the phlogopite lattice structure during crystallization. Therefore, a very high proportion of the strontium located in the phlogopite structure is ^{87}Sr produced by radioactive decay. Unaltered phlogopite in kimberlite occurs as bronze-colored macrocrysts/megacrysts (>5 mm in size), and/or as a groundmass mineral (<1 mm), and is commonly interpreted to have crystallized directly from the kimberlite magma. Figure 1d is an example of a phlogopite megacryst within Monastery kimberlite with well-developed cleavage. Mineral inclusions of perovskite and spinel are common. One cautionary note is that mica in kimberlite can also be xenocrystic, originating from disaggregated mantle or crustal xenoliths. In some cases mantle-derived phlogopite can still record the age of kimberlite eruption if the analyzed material resided at great depth in the mantle where radiogenic strontium could easily diffuse from the crystal until entrained by the kimberlite magma and transported to the surface. This would explain the identical Rb-Sr age results obtained for Wesselton groundmass phlogopite and phlogopite isolated from an entrained peridotite xenolith in the kimberlite (Allsopp and Barrett 1975). Although it is uncommon for both isotopic and geochemical information of analyzed phlogopites to be reported in the same study, several researchers have shown that the chemical composition of primary kimberlitic phlogopite is quite variable (e.g., Smith et al. 1978; Hunter et al. 1984; Mitchell 1986) but is distinct from phlogopite occurring in mantle xenoliths (Dawson and Smith 1975; Carswell 1975); noteworthy are the higher BaO, TiO_2 , and Al_2O_3 contents in the former.

Some of the early Rb-Sr phlogopite studies (e.g., Allsopp and Barrett 1975) noted that there is higher than expected common Sr contents in phlogopite. This led Brown et al. (1989) to develop an HCl leaching procedure that effectively removes the labile common Sr component within phlogopite (leaching in 1–2 N HCl at room temperature for 10–30 min). The explanation for the success of this treatment is that Sr-rich minerals, such as calcite, can occur along phlogopite cleavage planes (either as a primary magmatic or secondary alteration mineral) and the leaching step helps to dissolve and remove this common Sr component without influencing lattice-bound Rb and radiogenic Sr. Kimberlitic phlogopite can also be completely or partially altered to chlorite, and in these cases the analyses have significantly lower $^{87}\text{Rb}/^{86}\text{Sr}$ values than pristine phlogopite, increasing the uncertainty in the accuracy of the age determination.

Rb-Sr phlogopite dating of kimberlites and mantle xenoliths has been employed for more than 40 years, and over this time three approaches have been used: (1) phlogopite model dates, (2) combined phlogopite-whole rock “isochron” dates, and (3) phlogopite isochron dates. The procedure used in all Rb-Sr phlogopite dating studies is isotope dilution thermal ionization mass spectrometry where the selected material and a measured amount of a calibrated ^{87}Rb - ^{84}Sr tracer solution are combined in a Teflon digestion vessel together with a mixture of acids (5:1 $\text{HF}:\text{HNO}_3$) and heated on a hotplate for up to 48 h at 100 °C. Rb and Sr are purified using cation exchange chromatography and their isotopic compositions determined with a solid source thermal ionization mass spectrometer (Creaser et al. 2004). The precision of Rb-Sr phlogopite dates is typically better than 1 %, especially when the HCl leaching is conducted.

Phlogopite Rb-Sr Model Dates

As a result of the contrasting geochemical behavior of Rb and Sr in phlogopite, unaltered phlogopite typically has very high parent/daughter ratios ($^{87}\text{Rb}/^{86}\text{Sr} > 100$), and the highest

parent/daughter ratios are relatively insensitive to the choice of initial strontium isotopic composition. In samples where there is very little material to work with, a single Rb-Sr phlogopite analysis can be used to calculate a model date that is based on an estimate of the initial strontium isotopic composition. For example, if two possible $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio values of 0.705 and 0.710 are considered, then for phlogopites with $^{87}\text{Rb}/^{86}\text{Sr} > 300$ the shift on the model date is $\sim 0.3\%$, whereas for $^{87}\text{Rb}/^{86}\text{Sr} < 150$ the effect is $> 1\%$ depending on the assumed initial strontium isotopic value. For example, the phlogopite Rb-Sr model date of 50.8 Ma reported for the Grizzly pipe, NWT (Creaser et al. 2004), assuming an $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio of 0.705, increases to 52.8 Ma if the perovskite strontium isotope composition of 0.7043 is used to constrain the kimberlite magma composition (Sarkar et al. 2014).

Phlogopite-Whole Rock “Isochrons”

In some studies the age of kimberlite emplacement is estimated by measuring the Rb-Sr composition of both phlogopite (high Rb-Sr) and host kimberlite (low Rb-Sr), essentially using the whole rock kimberlite strontium isotopic composition as a proxy for the composition of the magma and the isotopic composition of phlogopite when it formed. The advantage of this approach is the significant reduction in the age uncertainty as multiple phlogopite analyses from a single sample may have low Rb-Sr or may not show a significant range in Rb-Sr. In one example from the Mark kimberlite in the Lac de Gras field, NWT, Davis and Kjarsgaard (1997) showed that three phlogopite analyses yielded an isochron age of 48 ± 7 Ma, whereas adding the whole rock kimberlite analyses yielded a similar age of 47.5 ± 0.5 Ma but with a reduced age uncertainty by nearly an order of magnitude. Some caution should be considered in interpreting these dates; whole rock kimberlite can contain a significant component of crust and/or mantle contamination which could yield a strontium isotopic composition that is not an accurate estimate for the kimberlite magma. The use of hypabyssal kimberlite is preferred as the whole rock anchor as this type of kimberlite typically contains the least amount of contamination. A better choice to anchor the isochron is to use a low $^{87}\text{Rb}/^{86}\text{Sr}$ mineral that crystallizes directly from the kimberlite magma. An ideal choice here would be groundmass perovskite (CaTiO_3); perovskite contains abundant strontium (> 500 ppm) and very low Rb (< 0.01 ppm) contents so there is negligible in-growth of radiogenic strontium. In most cases, groundmass perovskite faithfully records the primary kimberlite magma strontium isotopic composition (Heaman 1989), but there are examples where perovskite records a more complex crystallization history (Malarkey et al. 2010).

Phlogopite “Isochrons”

The Rb-Sr phlogopite “isochron” approach involves analyzing multiple aliquots from a single phlogopite megacryst or analyzing several phlogopite megacrysts from a single kimberlite. For this approach to be valid, the analyzed phlogopite megacrysts must have the same age, same initial strontium isotope composition, and be undisturbed by secondary post-crystallization (alteration). An example of the high precision that can be achieved using this method is the 59.7 ± 0.4 Ma (MSWD = 0.5) eight-point phlogopite isochron date reported for the Cobra South kimberlite, Lac de Gras field (Creaser et al. 2004). In this example the phlogopite analyses from four megacrysts displayed a large range in $^{87}\text{Rb}/^{86}\text{Sr}$ (28–281). With this level of precision, it is possible to investigate the detailed timing of kimberlite emplacement within a field or even a single pipe.

For example, based on high-precision Rb-Sr phlogopite dating of 27 Lac de Gras kimberlites, Creaser et al. (2004) documented at least four pulses of kimberlite magmatism occurred between 61 and 48 Ma.

Summary

Kimberlites are complex rocks containing a variety of minerals and rock fragments that either crystallized directly from the kimberlite magma, formed during alteration syn- and post-emplacment, or were entrained during transport of the magma to the surface from great depths in the mantle. As such, determining accurate emplacement ages for kimberlites has been challenging, especially by any whole rock dating technique. The U-Pb and Rb-Sr techniques have been successfully applied to minerals that are known to crystallize directly from the kimberlite magma (e.g., phlogopite and perovskite) or to have formed in the mantle but remained at temperatures higher than the closure temperature to diffusion of daughter elements until entrained in the kimberlite magma and carried rapidly to the crust (e.g., mantle zircon). Determining the temporal evolution of kimberlite emplacement is key to understanding the triggering mechanism for this magmatism and can constrain their geodynamic setting (Heaman and Kjarsgaard 2000; Heaman et al. 2003, 2004).

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^{210}Pb Dating

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Keywords

Geochronology; Radioactivity; Radionuclide; Mass accumulation rates; Sedimentation rates

Synonyms

[Mass accumulation rates](#); [Recent sediment dating](#); [Sedimentation rates](#)

Definition

Method of dating recent sediment deposition and accumulation using down-core profiles of short-lived radioactive ^{210}Pb .

History

Roughly 50 years ago, a small group of scientists from Belgium and the USA, trying to better constrain ice sheet accumulation rates, attempted to apply what was then known about environmental lead as a potential geochronometer. Thus Goldberg (1963) developed the first principles of the ^{210}Pb dating method, which was soon followed by a paper by Crozaz et al. (1964), who examined accumulation history of Antarctic snow using ^{210}Pb . Shortly thereafter, Koide et al. (1972, 1973) adapted this technique to unravel sediment deposition and accumulation records in deep-sea environments. Serendipitously, they chose to work in a deep basin off California, where an independent and robust age model had already been developed. Krishanswami et al. (1971) extended the use of this technique to lacustrine deposits to reconstruct depositional histories of lake sediment and, maybe more importantly, contaminant inputs and burial. Thus, the powerful tool for dating recent (up to about one century old) sediment deposits was established and soon widely adopted. Today almost all oceanographic or limnologic studies that address recent depositional reconstructions employ ^{210}Pb as one of several possible geochronometers (Andrews et al. 2009; Gale 2009; Baskaran 2011; Persson and Helms 2011). This entry presents a short overview of the principles of ^{210}Pb dating and provides a few examples that illustrate the utility of this tracer in contrasting depositional systems. Potential caveats and uncertainties (Appleby et al. 1986; Binford 1990; Binford et al. 1993; Smith 2001; Hancock et al. 2002) inherent to the use and interpretation of ^{210}Pb -derived age models are also introduced. Recommendations as to best practices for most reliable uses and reporting are presented in the summary.

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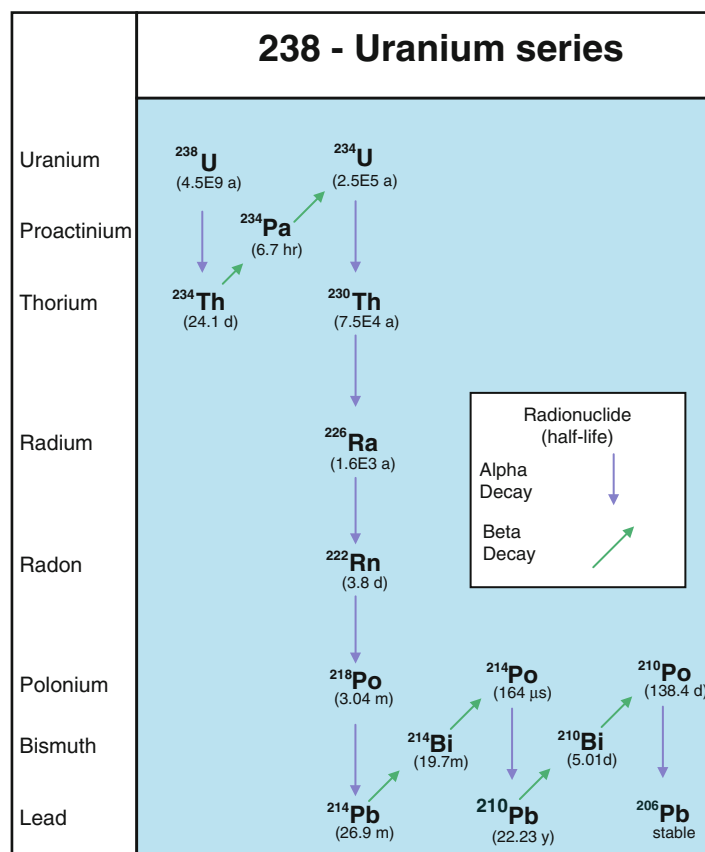


Fig. 1 The ^{238}U decay chain showing ^{226}Ra , ^{222}Rn , ^{210}Pb , and ^{210}Po . Half-lives are shown in parentheses where *a* years, *d* days, *hr* hours, *m* minutes, and μs microseconds

^{210}Pb Dating Principles

Pb-210 is a naturally occurring radionuclide of the ^{238}U radioactive decay chain and has a half-life ($t_{1/2}$) of 22.23 years (Fig. 1). In most environmental systems that have remained “closed” for more than about 120 years (five times the half-life of ^{210}Pb), ^{210}Pb is derived from its parent radionuclide, ^{226}Ra ($t_{1/2} = 1,600$ years), that is present in the material will reach a state of radioactive secular equilibrium. In such settings, ^{210}Pb is not a viable geochronometer. However, in more recently deposited sediment, ^{210}Pb may not be in equilibrium with parent isotope ^{226}Ra and may have an additional source unrelated to ^{226}Ra . First, a fraction of the observed ^{210}Pb is continuously produced by decay of ^{226}Ra and represents “supported” ^{210}Pb , which is considered time independent. The second fraction originates from the decay of atmospheric ^{222}Rn into ^{210}Pb and is called “excess” ^{210}Pb . After wet/dry deposition, rapid scavenging processes remove this radionuclide from the water column (Chanton et al. 1983; Crusius and Anderson 1995) via adsorption onto suspended particulates which may then become incorporated in sediment (Fig. 2). Bottom sediment thus contains a mixture of both supported and excess ^{210}Pb . This excess ^{210}Pb predictably decays with its 22.23 year half-life and can be used to establish recent sediment geochronologies (Goldberg and Bruland 1974; Appleby and Oldfield 1983) under ideal depositional conditions.

If both sediment accumulation and the flux of excess ^{210}Pb to a sediment surface are constant over time, and there are no postdepositional processes that redistribute excess ^{210}Pb present in the sediment, then a down-core profile of excess ^{210}Pb will follow a simple exponential curve that

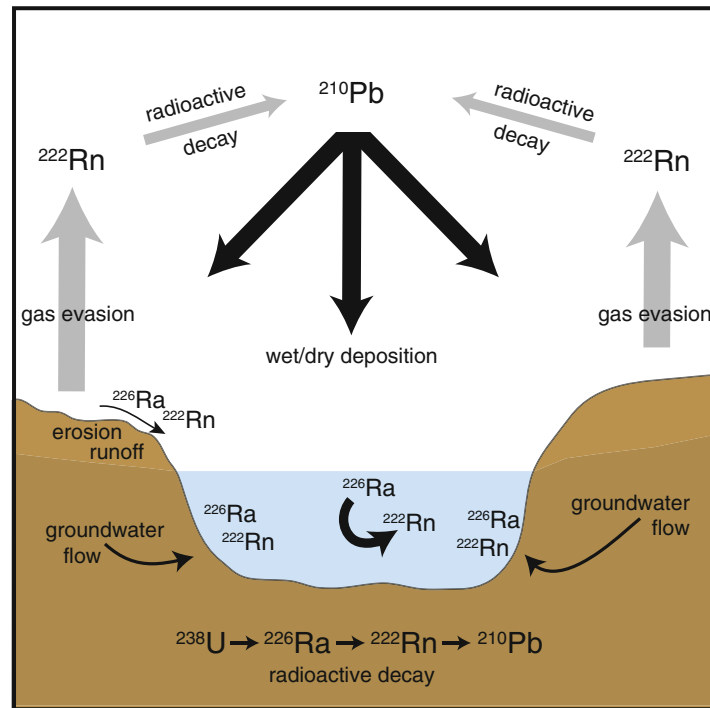


Fig. 2 Conceptual illustration of the dominant sources and transport pathways for ^{210}Pb

tracks its decay. Although these two assumptions are not always observed in natural settings, this simple premise forms the underlying principle for use of ^{210}Pb as a geochronometer. More intricate models have been developed that address nuances in the flux of sediment and ^{210}Pb (Sanchez-Cabeza and Ruiz-Fernandez 2012), as well as the effects of postdepositional mixing (Pourchet et al. 1989), including bioturbation (Benninger et al. 1979; Nittrouer et al. 1983).

Goldberg (1963) first proposed the constant flux model, where the ^{210}Pb flux to sediment is assumed to be constant over time, while the sedimentation rate may vary. This model subsequently became known as the constant rate of supply (CRS) model (Appleby and Oldfield 1978; Benoit and Rozan 2001; Robbins 1978), which is still one of the most often used ^{210}Pb dating models (Sanchez-Cabeza et al. 2000; Persson and Helms 2011). This model assumes that the down-core excess ^{210}Pb activity, vertically integrated to a depth, x , or a cumulative dry mass, m , will equal the flux integrated over the corresponding time interval. Integrating to either x or m ,

$$A(x, m) = A_0 e^{-\lambda t} \quad (1)$$

where $A(x, m)$ is the cumulative residual unsupported or excess ^{210}Pb activity beneath sediment of depth x , or mass m , A_0 is the total unsupported ^{210}Pb activity in the sediment column, λ is the ^{210}Pb decay constant, $0.03114 \text{ year}^{-1}$, and t represents time. The age of sediment at depth x , m is then described by:

$$t = \left(\frac{1}{\lambda} \right) \ln \left[\frac{A_0}{A(x, m)} \right] \quad (2)$$

Unlike the CRS model, in the constant initial concentration (CIC) model, the ^{210}Pb supply varies directly in proportion to the sedimentation rate (Shukla and Joshi 1989). Here the age (t) of a sediment layer is related to the depth (m) by

$$t = m/s \quad (3)$$

where m denotes the mass depth in the core (g cm^{-2}) and s denotes the sedimentation rate ($\text{g cm}^{-2} \text{ year}^{-1}$). The unsupported ^{210}Pb activity ($A(m)$) will thus vary with depth in accordance with the formula:

$$A(m) = A(0)e^{-\lambda m/t} \quad (4)$$

where λ is the decay constant and $A(0)$ is the unsupported activity at the surface of the core. When plotted on a logarithmic scale, the resulting ^{210}Pb activity versus depth profile will appear linear, and the mean sedimentation rate, s , can then be determined using a least squares fit procedure. With these simple equations, ^{210}Pb often can be used as a reliable geochronometer under suitable depositional conditions, although volumes have been written on more elaborate models and their limitations.

Many processes influence the delivery of excess ^{210}Pb to the bottom sediment of a lake or ocean. For example, the atmospheric flux of ^{210}Pb varies by latitude, altitude, and season (Garcia-Orellana et al. 2006; Baskaran and Swarzenski 2007). Catchment size and geology impact scavenging efficiencies and ensuing transport rates of ^{210}Pb (Nittrover et al. 1983). Water column depth and residence times and suspended particle composition may also affect ^{210}Pb cycling (Turner and Delorme 1996). Based on Appleby (2008), the CRS model will likely produce valid geochronologies if sediment transport rates from the catchment are reasonably constant and produce a minor component of supported ^{210}Pb compared to atmospheric flux rates contributing to excess ^{210}Pb .

^{210}Pb Measurements

Traditionally, the analytical determination of ^{210}Pb was based on either radiochemical separation of ^{210}Pb and measurement of its short-lived beta-emitting daughter, ^{210}Bi ($t_{1/2} = 5.01$ day), or on alpha spectrometry of its indirect decay product ^{210}Po ($t_{1/2} = 138.4$ day) that was assumed to be in secular equilibrium with ^{210}Pb . While both of these methods are laborious, today's alpha-spectrometric systems often consist of sophisticated, integrated sets of multiple detectors so one sediment core can theoretically be counted in just a few days. Advanced planar- or well-type semiconductor detectors enable the gamma-spectrometric analysis of the 46.5 keV decay energy of ^{210}Pb with high relative efficiency (Zaborska et al. 2007). Because gamma analysis of sediment requires only minor (nondestructive) laboratory work, the use of gamma detectors has considerably reduced the effort for most routine ^{210}Pb determinations. In addition, the gamma-spectrometric method provides a concurrent determination of ^{226}Ra , which allows the activities of supported ^{210}Pb to be estimated. Ra-226 activity is determined by quantifying intermediate daughter radionuclides ^{214}Pb (at 295 and 352 keV) and ^{214}Bi (at 609 keV) after establishing their radioactive equilibrium with ^{222}Rn (Kirchner and Ehlers 1998; Swarzenski et al. 2006). Importantly, the gamma-spectrometric method also provides for the determination of ^{137}Cs ($t_{1/2} = 30.17$ year; 661 keV), an independent, nuclear bomb-produced geochronometer.

Based on our own laboratory experience, detection limits for ^{210}Pb are typically less than 10 mBq g^{-1} for well-type HPGe gamma detectors and are likely somewhat lower for planar

detectors that can accommodate much larger sediment sample sizes (~20–50 g). Thus, detection limits for gamma detectors may be considerably higher than those achievable with alpha-spectrometric counting of radiochemically separated ^{210}Po . As a consequence, gamma spectrometry may be of limited use in areas showing small atmospheric deposition rates of ^{210}Pb .

Prior knowledge of the analytical detection limits of the instrumentation as well as the sample size and geometry can affect the decision on how to best section a sediment core for ^{210}Pb analyses (Kirchner 2011). Because of the inverse relationship between particle surface area and particle size, muddy sediment usually contains the highest activities of adsorbed ^{210}Pb (Smith and Walton 1980). Thinner sediment layers expectedly provide a better time resolution of sedimentation rates but may compromise counting statistics if there is not enough excess ^{210}Pb present within a sediment layer. For a given flux of excess ^{210}Pb into the sediment, its activity concentrations are inversely related to the sedimentation rate (Alexander and Lee 2009). Thus, some prior estimate of the expected sedimentation rate is also desirable to guide the core sectioning. An independent estimate of sedimentation rate may be available, for example, from lithological analyses of the core (i.e., varves). Otherwise, the core should be sectioned into thin, consecutive layers and, starting with the youngest sediment, measured layer by layer until excess ^{210}Pb activities approach parent-supported activities. If ^{210}Pb activities approach instrument detection limits, the sediment layers can be combined prior to analysis.

After sectioning, each sediment layer is homogenized and weighed prior to and after drying at 105 C for at least 24 h (Swarzenski et al. 2006). The wet and dry weights provide water content information. The porosity (ϕ) of each sample is calculated as follows:

$$\phi = f_w / [f_w + (1 - f_w)\rho_w / \rho_s] \quad (5)$$

where f_w is the fraction of water in the wet sediment ($=1 - \text{dry wt.}/\text{wet wt.}$), ρ_w is the density of pore water (assumed to be 1.0 g cm^{-3}), and ρ_s is the density of dry sediment particles (assumed to be 2.5 g cm^{-3}). The cumulative mass depth (M) is calculated as follows:

$$M(\text{mg cm}^{-2}) = \sum [1 - \phi_i)\rho_s \delta x \quad (6)$$

where ϕ_i is the porosity at depth “ i ” and δx is the thickness of the layer (i.e., 1 cm). The dried sediment layers are pulverized using an agate mortar and pestle and prepared for subsequent analyses.

Three Examples of ^{210}Pb Profiles in Diverse Depositional Settings

Submarine basin – The San Pedro Basin is located in the Southern California Bight, adjacent to Los Angeles, California, USA. This marine basin acts as an efficient trap for both natural and anthropogenic materials. Due to the bathymetry of this deep basin, water circulation is restricted and, as a consequence, water residence times are long. Such a depositional setting is ideal for excess- ^{210}Pb -derived geochronologies. Previous work on sedimentation rates in the San Pedro Basin (Huh et al. 1990; Alexander and Lee 2009) corroborate the excess ^{210}Pb and ^{137}Cs geochronology shown in Fig. 3. Both down-core profiles of ^{137}Cs and excess ^{210}Pb indicate that the sediment has been accumulating at a rate close to 0.09 cm day^{-1} ; although finer scale sectioning would likely show a decline in the sedimentation rates around the turn of the twentieth century, coincident with intensified sediment discharge controls on land.

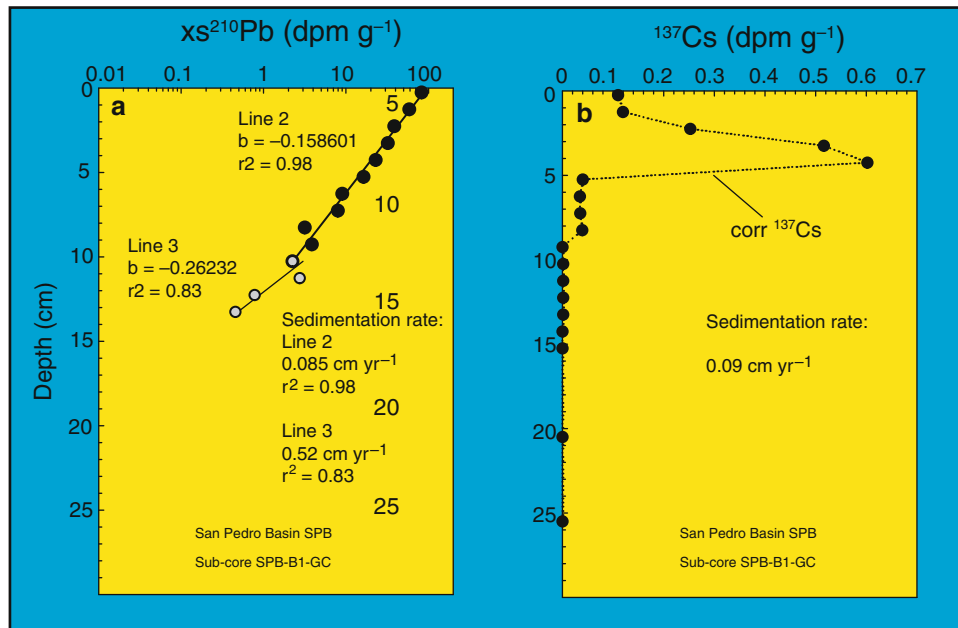


Fig. 3 (a) Excess down-core ^{210}Pb ($x\text{s}^{210}\text{Pb}$) and (b) ^{137}Cs profiles (in disintegrations per minute, dpm) and derived sedimentation rates in a deep submarine basin: San Pedro Basin, California. $60 \text{ dpm} = 1 \text{ Bq} = 27.027 \text{ pCi}$. In (a) *black* and *gray* symbols distinguish unique linear sediment rates. Summary parameters of the linear regression are represented as the slope (b) and r-squared (r^2) value

Alpine lake – Copper Lake is located in the North Cascades National Park, Washington State, less than 10 km from the USA-Canada border (Sheibley et al. 2012). The lake is at an elevation of about 1,600 m above mean sea level and has a surface area of 5.2 ha. The maximum depth of the lake is about 20 m. Figure 4 shows the down-core profiles of excess ^{210}Pb and ^{137}Cs for Copper Lake. The activities of both ^{137}Cs and excess ^{210}Pb are high and indicative of large atmospheric fluxes being delivered into a small basin.

Sinkhole lake – Lake Tulane (40 ha) is located in central Florida at an elevation of 35 m above mean sea level and contains one of the longest climate records for a lake in the USA (Grimm et al. 1993). As a sinkhole lake, Lake Tulane was formed when a limestone deposit catastrophically collapsed due to dissolution by groundwater. Today, the water budget of the lake is balanced by surface and groundwater contributions. Sustained groundwater seepage can also transport radionuclides such as ^{226}Ra . Figure 5 shows the down-core profiles of excess ^{210}Pb and total (supported) ^{210}Pb for Lake Tulane. There is a pronounced mixed layer – ubiquitous in sediment that contains an active biological community – which extends down to $\sim 10 \text{ cm}$. Excess ^{210}Pb systematically declines down core to yield two solid sedimentation rates, but at a depth of $\sim 40 \text{ cm}$, there is a notable inflection in the total (supported) ^{210}Pb activities. It is likely that this down-core anomaly is produced from ^{226}Ra -rich groundwater seepage (Brenner et al. 2004). Norton et al. (1985) concluded that similar anomalies observed in several high-altitude alpine lakes in Rocky Mountain National Park, Colorado, were the result of groundwater movement that likely impacted the distribution of ^{210}Pb .

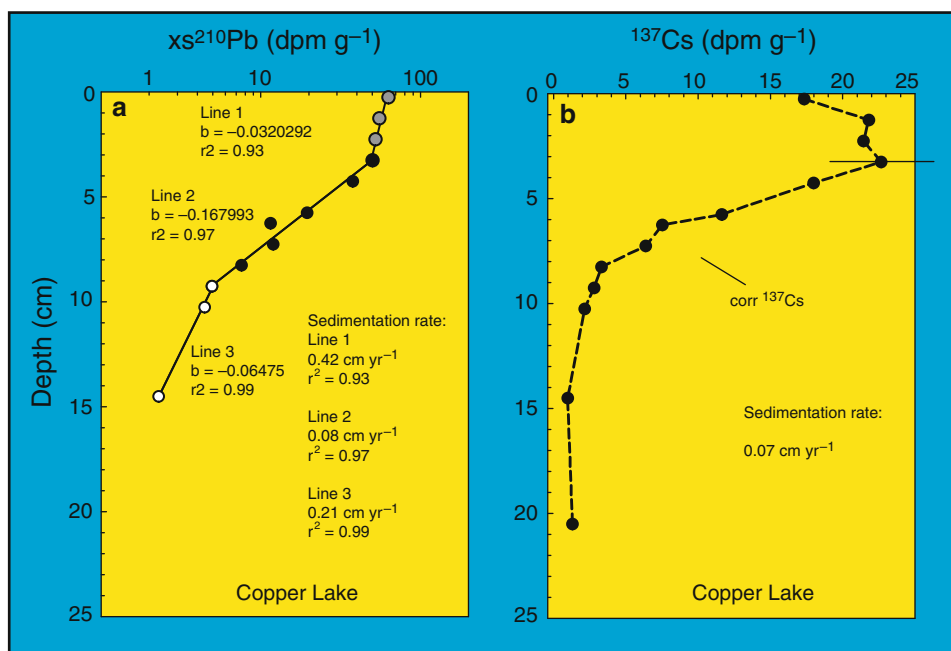


Fig. 4 Excess ^{210}Pb and ^{137}Cs down-core profiles and derived sedimentation rates in an alpine lake: Copper Lake, Washington (Redrawn from Sheibley et al. 2012). In (a) white, black, and gray symbols distinguish unique linear sediment rates. Summary parameters of the linear regression are represented as the slope (b) and r-squared (r^2) value

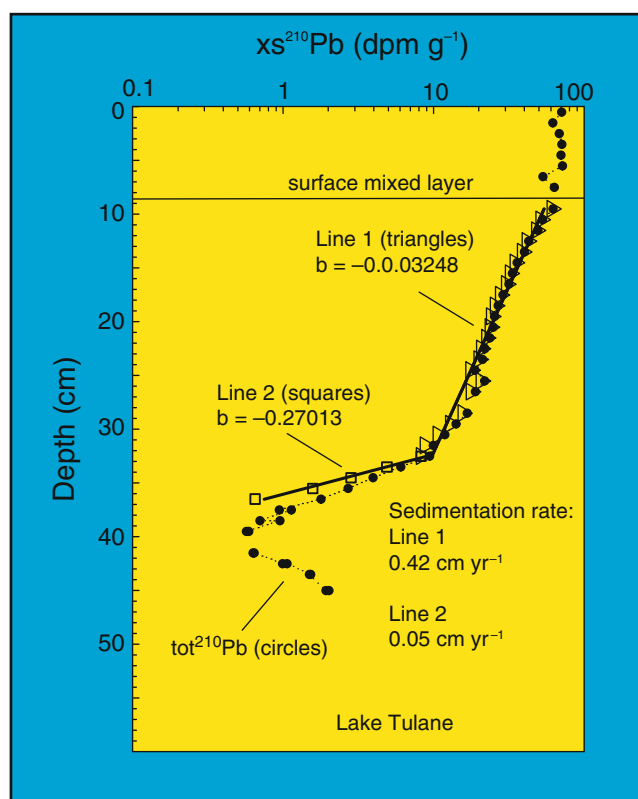


Fig. 5 Excess ^{210}Pb (xs^{210}Pb) and total (supported) ^{210}Pb ($\text{tot}^{210}\text{Pb}$, solid black circles) down-core profiles and derived sedimentation rates in a sinkhole lake: Lake Tulane, Florida. Open triangles (Line 1) and open squares (Line 2) distinguish unique linear sediment rates. Summary parameters of the linear regression are represented as the slope (b)

Summary

During the last decade, there has been an unprecedented push to learn more about how the environment has changed over time. This interest is grounded in trying to better understand differences between natural- and anthropogenic-driven changes and how our environment may respond to such changes in the future. One of the most fundamental steps in establishing a record of environmental change is to first derive an accurate geochronology. The geochronologies generated by ^{210}Pb analysis can resolve the very recent past (last 100–200 years), with total (1σ) uncertainties varying from just under 1 year to around a decade (Baskaran 2011). However, ^{210}Pb geochronologies are not without inherent problems and uncertainties (Robbins and Edgington 1975; von Gunten and Moser 1993). The development of a ^{210}Pb geochronology should never become a routine exercise (Appleby and Oldfield 1992; Appleby 2008). Even some recent studies that employ ^{210}Pb as a geochronometer still fail to meet the minimum requirements identified by Oldfield and Appleby (1984). For example, some of these efforts may fail to adequately evaluate inconsistencies in competing ^{210}Pb models, or they may forego assessing ^{210}Pb model results against independent geochronologies (e.g., other radioisotope systems or varve counting). Lastly, some ^{210}Pb applications may ignore postdepositional mixing (Benninger et al. 1979; Berner 1980; Miguel et al. 2003) that can yield a surprisingly plausible down-core ^{210}Pb profile but which produces a geochronological model that is simply invalid (Kirchner 2011). That said, a carefully developed ^{210}Pb geochronology, and one substantiated in the peer-reviewed literature per recommendations outlined in Smith (2001) and Hancock et al. (2002), is invaluable in any recent environmental reconstruction. Sediment dating using ^{210}Pb methods will continue to be refined with new improvements in analytical and model capabilities.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Lacustrine Varves](#)
- ▶ [Marine Varves](#)
- ▶ [Sediment Mixing Rate, \$^{210}\text{Pb}\$](#)
- ▶ [U-Series Dating](#)
- ▶ [Varve Chronology](#)

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U-Series Dating

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Synonyms

^{231}Pa - ^{235}U dating; ^{226}Ra - ^{230}Th dating; ^{230}Th - ^{238}U dating; ^{238}U - ^{234}U dating; Uranium-series disequilibrium dating

Definitions

Uranium series: Any of the radioactive decay products produced from either of two long-lived isotopes of uranium (U) found in nature (^{238}U and ^{235}U) resulting in a sequence of shorter-lived radioactive daughter isotopes that can be used to provide age information based on the well-characterized decay constants for each isotope in the decay series and the fact that they can be fractionated due to differences between their chemical or nuclear properties.

Introduction

Over the past few decades, uranium decay series has emerged as a fundamental tool for dating recent geological events with an extremely wide range of applications. There have been several recent reviews about the geochronological applications of these isotopic tools (e.g., Bourdon et al. 2003). This entry presents first the analytical methods with a special focus on new techniques, the basic principles, and a few classical applications. Following that, we focus particularly on new applications in the field of low-temperature geochemistry and storage of minerals in magma chambers. Overall, it can be stated with some confidence that U-series dating has become a method that has brought fundamental advances in several subfields of Earth sciences dealing with recent processes. It is beyond the scope of this entry to give a comprehensive picture of all the applications that are available. Rather, the focus here is on the methodological aspects of this dating technique.

Basic Principles in U-Series Nuclide Dating

Dating based on U-series nuclides was an idea that was first introduced by Piggot and Urry in 1942, and most methods rely on relatively similar principles. There are two U-series decay chains: (1) ^{238}U decays to stable ^{206}Pb via a series of alpha and beta decays, whereas (2) ^{235}U decays to stable ^{207}Pb . In the case of a long-lived nuclide such as ^{238}U or ^{235}U (half-lives of ~ 4.5 Ga and 0.7 Ga, respectively), it has been shown by Bateman (1910) that after a time equivalent to six times the half-life of the longest-lived daughter, the U-decay chain reaches a state of secular equilibrium defined by an equality of all activities:

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$$\lambda_1 N_1 = \lambda_2 N_2 = \dots = \lambda_n N_n \quad (1)$$

where the subscript 1 indicates the parent nuclide (^{238}U or ^{235}U), λ_i is the decay constant for nuclide i , and N_i is the number of nuclides of i . The symbols used throughout this entry are given in Table 1. The intermediate daughter nuclides can fractionate from their parent nuclide owing either to different nuclear properties (e.g., ^{238}U – ^{234}U) or due to different chemical properties, which are used in most applications. If there is a fractionation between two nuclides in the chain, there is a so-called radioactive disequilibrium in the decay chain. The return to secular equilibrium is a function of time, and this property can be used for age determination (see Fig. 1). This principle is similar to other radiometric dating methods. However, in the case of U-series nuclides, the fact that the nuclides are short lived and produced by a parent nuclide (i.e., ^{238}U or ^{235}U) which is itself radioactive introduces an additional complexity. This means that following a fractionation event between two given nuclides, the dating method can only be operative as long as there is a detectable difference between the value measured for the daughter nuclide and the value reached at secular equilibrium, which is usually of the order of six half-lives. The dating methods based on U series can be divided into three main types that are described below (see a compilation in Table 2).

Table 1 Symbols used in the equations

Parameter	Meaning
D	Fractal dimension of mineral surface
f_α	Fraction of ejected daughter nuclides
λ_8	Decay constant of ^{238}U
λ_4	Decay constant of ^{234}U
λ_0	Decay constant of ^{230}Th
k_i	Release rate of nuclide i in year^{-1}
Q_α	α -Decay energy
M	Atomic mass

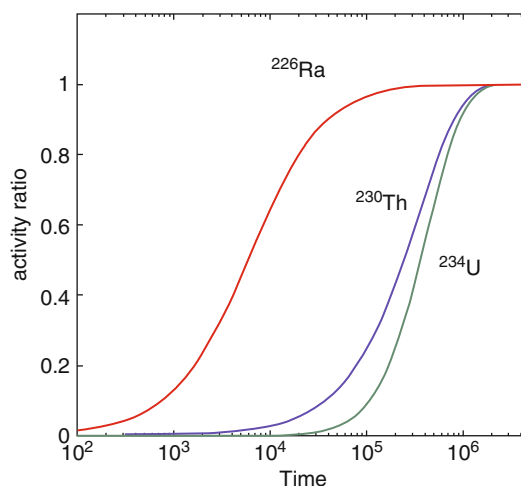


Fig. 1 Diagram showing the concept of secular equilibrium for ^{234}U , ^{230}Th , and ^{226}Ra and the time it takes for each to return to secular equilibrium starting from an activity ratio (with respect to ^{238}U) equal to zero

Table 2 Overview of U-series dating methods

Object to be dated	Method	Analytical technique	Age range	Indicative reference
Volcanic rocks	^{230}Th – ^{238}U	MC-ICP-MS	0–300,000 years	Condomines et al. (2003)
Phenocrysts	^{226}Ra /Ba– ^{230}Th	MC-ICP-MS, TIMS	0–10,000 years	Cooper et al. (2001)
Magma storage	^{226}Ra – ^{230}Th	MC-ICP-MS, TIMS	0–10,000 years	Vigier et al. (1999)
Accessory minerals	^{230}Th – ^{238}U	SIMS, LA-ICP-MS	0–300,000 years	Schmitt (2011)
Authigenic carbonate	^{230}Th – ^{238}U , ^{234}U – ^{238}U	MC-ICP-MS, LA-ICP-MS	0–10 ⁶ years	Cheng et al. (2013)
Gypsum	^{230}Th – ^{238}U , ^{234}U – ^{238}U	MC-ICP-MS	0–10 ⁶ years	Sanna et al. (2010)
Authigenic opal	^{230}Th – ^{238}U	SIMS, TIMS	0–300,000 years	Paces et al. (2004)
Fe/Mn oxy-hydroxide	^{230}Th – ^{238}U	LA-ICP-MS	0–300,000 years	Bernal et al. (2006)
Bone (apatite)	^{230}Th – ^{238}U	MC-ICP-MS	0–300,000 years	Grün et al. (2010)
Recent carbonates	^{226}Ra –Ba	TIMS, MC-ICP-MS	0–10,000 years	Staubwasser et al. (2004)
Ice core	^{234}U recoil	MC-ICP-MS	0–800,000 years	Aciego et al. (2011)
Young sediments	^{210}Pb	γ -Spectroscopy	0–100 years	Appleby and Oldfield (1978)

MC-ICP-MS multi-collector inductively coupled mass spectrometry

TIMS thermal ionization mass spectrometry

SIMS secondary-ion mass spectrometry

LA-ICP-MS laser ablation inductively coupled mass spectrometry

Dating Based on ^{238}U – ^{234}U Disequilibrium

The main principle behind the ^{238}U – ^{234}U dating method is that in low-temperature environments, ^{234}U is likely to fractionate from ^{238}U . The first part of the ^{238}U decay chain can be written as follows:



For most geological processes, the half-lives of ^{234}Th and ^{234}Pa are very short (24.1 days and 6.69 h, respectively). The cause of the fractionation between ^{234}U and ^{238}U is that the α -decay of ^{238}U is accompanied by a recoil displacement of the daughter nuclide (^{234}Th) during ejection of the α particle (helium nucleus). One can calculate the kinetic energy of the recoil nuclide assuming conservation of momentum of the two nuclides and show that it is a fraction of the total energy depending on the relative masses of the helium and the ^{234}Th atoms:

$$E_c^{234}\text{Th} = Q_\alpha \frac{M_\alpha}{M_\alpha + M_{234}\text{Th}} \quad (3)$$

where Q_α is the total energy of decay and M_α and $M_{234}\text{Th}$ are the masses of ^4He and ^{234}Th , respectively. The ^{234}Th is ejected from the site where ^{238}U had formerly resided, and this can have various consequences. If the ^{238}U resided near the edge of a grain, the ^{234}Th can be ejected out of the grain. Alternatively, it can be leached out of the grain more easily during weathering reactions relative to the original ^{238}U because it no longer is in a stable lattice site. Collectively, these processes are called the Szilard effect, and their consequences during leaching have been shown experimentally by Kigoshi (1971) for zircons. Experiments by Andersen et al. (2009) using minerals

in granite also illustrated the effect of dissolution on ^{234}U – ^{238}U fractionation. This fractionation between ^{234}U and ^{238}U is the reason why many continental waters including rivers and aquifers have an excess of ^{234}U relative to ^{238}U and why seawater has an elevated ($^{234}\text{U}/^{238}\text{U}$) (parentheses designate activity ratio here and throughout this entry) equal to 1.14 (Andersen et al. 2010). As the residence of uranium in the ocean is relatively long (on the order of 1 Ma), this activity ratio has remained relatively constant over the past million years. If a mineral forms from seawater or any water whose ($^{234}\text{U}/^{238}\text{U}$) is known and subsequently behaves as a closed system, the following equation can be used to calculate its isotopic evolution with time:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_t - 1 = \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_{\text{initial}} - 1\right) e^{-\lambda t} \quad (4)$$

This equation can be inverted to obtain the time since the mineral last equilibrated with water provided the initial ratio is known.

Dating Based on ^{230}Th – ^{238}U and ^{231}Pa – ^{235}U Disequilibrium

The principle of this dating method is somewhat different from the ^{238}U – ^{234}U dating method as the fractionation resulting in radioactive disequilibrium between nuclides of Th, Pa, and U is caused by differences in their chemical properties in various environments (Fig. 2). In high-temperature environments, Th, Pa, and U behave as incompatible elements that are too large to be incorporated quantitatively in most mineral sites (Blundy and Wood 2003). However, as the ionic radii of Th and Pa are slightly larger than U, the mineral/melt partition coefficient of U is slightly greater than that of Th and Pa in many minerals. During partial melting of the mantle or during crystallization of magmas, Th and Pa are partitioned preferentially into the liquid phase relative to U, which makes the dating of these processes possible. In most cases, one can date crystallization of magmatic rocks using the isochron method described below.

In low-temperature environments, the chemical behavior of U, Th, and Pa is also different as U can be mobile in oxidizing environments while Th and Pa remain rather immobile and insoluble (Langmuir 1978). This is due to the fact that U can be oxidized to U(VI), which forms a soluble species, UO_2^{2+} , by hydrolysis with water. In contrast, Pa(V) and Th(IV) are very insoluble and

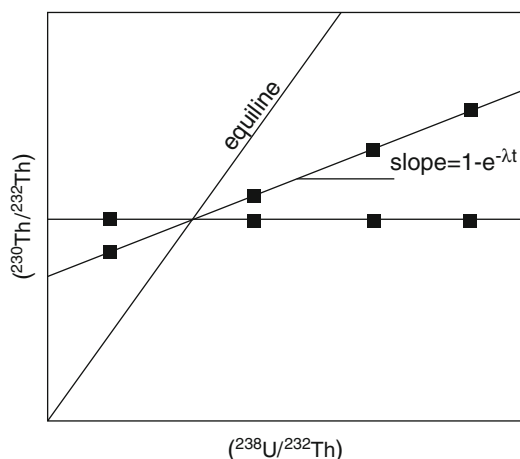


Fig. 2 Principle of ^{230}Th – ^{238}U isochron dating. The *black squares* represent a series of co-genetic samples characterized by an identical ($^{230}\text{Th}/^{232}\text{Th}$) ratio at $t = 0$. At time t , as each sample behaved as a closed system, they tend to return to secular equilibrium, i.e., ($^{230}\text{Th}/^{238}\text{U}$) = 1. The line of secular equilibrium is marked as the equiline

remain tightly bound to solids by adsorption. An important consequence is that U is enriched in seawater compared with Th, and in some authigenic (hydrogenic) minerals, U can be enriched while Th is virtually absent. All these characteristics often induce a large fractionation between Th, Pa, and U which is the basis for the ^{230}Th – ^{238}U and ^{231}Pa – ^{235}U dating methods.

Dating Based on ^{226}Ra – ^{230}Th Disequilibrium

As Ra and Th are also chemically distinct, they can fractionate from each other, which gives rise to various dating methods. In magmatic environments, it had been shown that Ra and Th have different partitioning behavior and since Ra has a larger ionic radius than Th, it is even more incompatible than Th in most minerals. There are, however, a few exceptions because some minerals have specific sites where +2 cations, such as Ca^{2+} , are favored. Recent experimental work has shown that the partition coefficients of Ra in plagioclase are greater than that of Th and that significant amounts of Ra can indeed be incorporated into this mineral (e.g., Fabbrizio et al. 2009).

Consequently, dating methods based on ^{226}Ra – ^{230}Th disequilibrium in minerals have been developed. Rubin and Macdougall (1990) and Volpe and Goldstein (1993) showed that if one assumes that Ra and Ba, both being large incompatible elements with +2 charges, are chemical analogs, then one can normalize the ^{226}Ra concentration by that of Ba and determine an age using an isochron method. The corresponding equation is similar to that used for ^{230}Th – ^{238}U isochron dating (see section [Dating Volcanic Rocks](#)).

Analytical Methods

Because of their low abundances in natural samples, the analytical methods used for measuring the daughter nuclides of U or Th require high sensitivity. Until the 1990s, the method of choice was nuclear spectrometry (alpha or gamma spectrometry), which was particularly well adapted for the analysis of the short-lived nuclides such as Ra, Po, or ^{210}Pb . However, for nuclides with a half-life exceeding a few thousand years (in particular ^{234}U , ^{230}Th , ^{231}Pa , or ^{226}Ra), the detection limit and duration of analysis make mass spectrometry a much more suitable method. The introduction of mass spectrometric methods for the analysis of these nuclides (Chen et al. 1986; Edwards et al. 1987) triggered a revolution in the sense that many applications have yielded substantially improved time resolution or has made possible a number of applications which only had marginal interest prior to collection of data by mass spectrometry. The first applications using mass spectrometric techniques employed thermal ionization mass spectrometry (TIMS), which enabled precise analysis of ^{234}U and ^{230}Th (Chen et al. 1986; Edwards et al. 1987) with detection limits of a few picograms for both U and Th. The basic methodology consisted of loading the Th- or U-bearing salts purified from digested solutions onto a single Re filament coated with a colloidal graphite solution for uranium or double/triple filament for Th (Goldstein and Stirling 2003).

An additional feature that made these analyses technically attractive was the development of high-abundance sensitivity filters. For the precise analysis of ^{230}Th , one issue is the large abundance of ^{232}Th relative to ^{230}Th . The collision of ^{232}Th ions with residual gas in the mass spectrometer creates a dispersion of energies causing formation of a tail on both sides of the ^{232}Th peak. In a standard magnetic-sector TIMS instrument, the abundance sensitivity around mass ^{232}Th is typically a few 10^{-6} at 1 amu, and this amount yields a significant contribution to the very much smaller ^{230}Th peak. The correction for this contribution is imprecise and produces significant errors on ^{230}Th measurements. In the nineties, new high-abundance sensitivity filters were developed, and these devices

improved the abundance sensitivity by a factor of approximately 10–100, which makes the correction negligible (Goldstein and Stirling 2003).

The TIMS method resulted in ion yields that ranged between 10^{-4} and 10^{-2} at most for U and Th (as compiled in Goldstein and Stirling 2003). Note that the larger figure given here (10^{-2}) was obtained for low amounts of U (or Th) loaded onto a filament. For many applications, this sensitivity was sufficient for samples with elevated U concentrations, but there could be analytical limitations for low-concentration samples (see section [Dating Volcanic Rocks](#)). In addition, the duration of the analysis (several hours each for separate U and Th runs) could be a limiting factor, particularly in cases where time series and large sample sets were important. This is particularly relevant in paleoclimate studies.

More recently, with the advent of multi-collector inductively coupled plasma mass spectrometry, or MC-ICP-MS (Luo et al. 1997; Turner et al. 2001), it has been possible to consistently obtain higher sensitivity (regardless of sample size) without compromising the abundance sensitivity. One should note, however, that the abundance sensitivity using the same filtering device as in TIMS was not as good owing to the differing ion properties in the TIMS and ICP-MS sources. In a TIMS source, the energy dispersion of the ions is limited to less than 1 eV, and thus, the abundance sensitivity filter, which sorts the ions according to their energy, works optimally. However, in the ICP-MS source, the energy dispersion of the ions out of the plasma is up to 10 eV, which means that the energy filtration is less efficient. As a result, for optimal collection with a yield greater than 90 %, the abundance sensitivity is typically 2×10^{-7} , which is usually sufficient for most analyses. As shown in Hubert et al. (2006), it is useful to determine the precise shape of the ^{232}Th tail for better precision of MC-ICP-MS analyses.

An additional feature that has emerged in the last few years is the possibility of measuring U-series disequilibria by laser ablation (LA) coupled to an ICP-MS, which affords considerable advantages for specific applications. Given that U and Th are generally present in minerals at trace abundances, it is a challenge to find samples for which the sensitivity of the LA-ICP-MS method is sufficient to yield reasonable uncertainties. The first convincing developments were done on samples with high U concentrations (a few hundred ppm) (Stirling et al. 2000; Eggins et al. 2005; Bernal et al. 2006). More recently, it has been shown that reliable results could be obtained dating coral with <5 ppm U using a 193 nm excimer laser coupled with an MC-ICP-MS (Potter et al. 2005). The main reason for using this frequency is that the elemental and isotope fractionation associated with this laser frequency is limited. It was hoped that the development of the femtosecond laser would also limit the degree of fractionation (Horn and von Blanckenburg 2007). A recent study of U–Th disequilibria in sphene using a femtosecond laser has shown that while the $^{230}\text{Th}/^{232}\text{Th}$ ratios could be measured accurately, it was more difficult to obtain precise results on Th/U ratios if the standard compositions did not match the matrix of the natural samples (Koornneef et al. 2012). Thus, an important conclusion from this research is that the production of high quality standards of equivalent composition and texture seems essential.

Classical Applications

Dating Volcanic Rocks

The most commonly used U-series method for dating volcanic rocks is based on ^{230}Th – ^{238}U disequilibrium. This represents an excellent alternative to the ^{14}C dating of charcoal associated with volcanic eruptions. With this disequilibrium method, the eruptive products themselves can be dated up to ages as old as 300,000 years. One should note, however, that the uncertainty in the age

determination is smaller for younger eruptions. For the purpose of this method, the assumption is made that there is no ^{234}U – ^{238}U disequilibrium caused by high-temperature processes. This assumption has most often been verified. An exception was described by Pietruszka et al. (2011) who found excess ^{234}U in volcanic rocks due to the effect of assimilation. For dating a specific eruption, one assumes that all the minerals formed from a given lava had uniform $^{230}\text{Th}/^{232}\text{Th}$ ratios and that all mineral phases remained closed to secondary mobility after cooling. One issue that has been pointed out numerous times is that some crystals may have actually grown earlier than the time of the eruption or that some crystals may be recycled (e.g., Bourdon et al. 1994). Overall, this method gives a reasonable approximation for the age of volcanic eruption. It has been possible in some cases to cross-check the validity of U-series ages with ^{14}C dating or $^{40}\text{Ar}/^{39}\text{Ar}$ dating.

The equation used for ^{230}Th – ^{238}U age determination is as follows:

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right) = \left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right)_0 e^{-\lambda t} + \left(\frac{^{238}\text{U}}{^{232}\text{Th}}\right) (1 - e^{-\lambda t}) \quad (5)$$

This equation can be used to fit a linear regression to a series of measurements of co-genetic samples in a $(^{230}\text{Th}/^{232}\text{Th})$ versus $(^{238}\text{U}/^{232}\text{Th})$ diagram (Allègre 1968). In this case, the slope can be used to yield an age via the following equation:

$$\text{Slope} = 1 - e^{-\lambda t} \quad (6)$$

For samples whose age is greater than about six half-lives of the daughter nuclide ^{230}Th (~450,000 years), the slope reaches a value indistinguishable from 1, in which case no age determination is possible.

Dating Authigenic or Biogenic Minerals

Upon formation of biogenic or authigenic carbonates, there is no incorporation of Th or Pa due to their low solubilities in aqueous solutions, while soluble U or Ra can be substituted into the CaCO_3 mineral lattice. As a consequence, the formation of carbonate leads to a large disequilibrium between ^{238}U and ^{230}Th and between ^{235}U and ^{231}Pa , which can be used for age determination. The equation for age determination when no initial ^{230}Th is present can be written as follows:

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right) = 1 - e^{-\lambda_0 t} + \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right) - 1\right) \left(\frac{\lambda_0}{\lambda_0 - \lambda_4}\right) (1 - e^{-(\lambda_4 - \lambda_0)t}) \quad (7)$$

In this equation, one makes the assumption that the $^{234}\text{U}/^{238}\text{U}$ ratio of the carbonate is known. If the carbonate is formed in equilibrium with seawater whose $^{234}\text{U}/^{238}\text{U}$ ratio arguably has remained constant over the last million years (Andersen et al. 2010), it is possible to have a cross-check of the ^{230}Th – ^{238}U age determination as the $^{234}\text{U}/^{238}\text{U}$ ratio decreases with time from its initial value inherited from seawater (see section [Dating Based on \$^{238}\text{U}\$ – \$^{234}\text{U}\$ Disequilibrium](#)).

In most cases, this ^{238}U – ^{234}U age is less precise than the ^{230}Th – ^{238}U or the ^{231}Pa – ^{235}U ages, but when the carbonates are older than about 150 kyr, the ^{238}U – ^{234}U method may become the best method to date carbonates (Andersen et al. 2008). In the case of marine carbonates, one important issue that controls the precision of the age is the extent to which the $^{234}\text{U}/^{238}\text{U}$ of the oceans has remained constant over time.

It has been found that in the case of relatively old corals, the methods described above do not produce reliable ages. Rather, there may be clear evidence for open-system behavior, and several

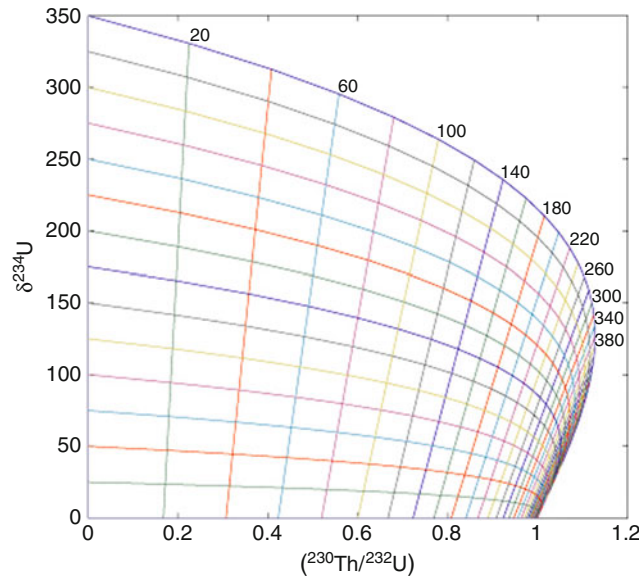


Fig. 3 Principle of concordia dating with ^{238}U – ^{234}U – ^{230}Th system for authigenic minerals such as carbonate. The notation $\delta^{234}\text{U}$, in per mil units, corresponds to $((^{234}\text{U}/^{238}\text{U}) - 1) \times 1,000$. At $t = 0$, the starting composition of the mineral is assumed here to have $(^{230}\text{Th}/^{238}\text{U}) = 0$. Each subhorizontal line corresponds to samples with initial $\delta^{234}\text{U}$ given on the y-axis. With increasing age, the samples evolve toward secular equilibrium ($\delta^{234}\text{U} = 0$, $(^{230}\text{Th}/^{238}\text{U}) = 1$). The subvertical lines (isochrons) correspond to samples of equal age

theoretical or empirical approaches have been derived to take into account the possible loss or addition of U (Cheng et al. 1998; Henderson 2002; Thompson et al. 2003). In what follows, we describe briefly the formalism adopted by Thompson et al. (2003) to describe open-system behavior. This open-system behavior can be described in a predictive manner by assuming it is due to the recoil effects during ejection of ^{234}Th and ^{230}Th . The differential equations describing the evolution of each U-series nuclide with time can be written as follows:

$$\begin{aligned} \frac{d^{238}\text{U}}{dt} &= -\lambda_8^{238}\text{U} \\ \frac{d^{234}\text{U}}{dt} &= -\lambda_4^{238}\text{U} + f_4\lambda_8^{238}\text{U} \\ \frac{d^{230}\text{Th}}{dt} &= -\lambda_0^{230}\text{Th} + f_0\lambda_4^{234}\text{U} \end{aligned} \quad (8)$$

where f_i represents the fraction of parent nuclide retained in the carbonate. This system of coupled linear differential equations can be solved analytically to calculate a time evolution of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ in the solid. It is possible that some samples may experience a loss of ^{234}U and ^{230}Th while others may gain these components. By analyzing a series of co-genetic samples, it may be possible to use this approach to derive a true age. Thompson et al. (2003) have shown that this method yielded reliable ages for old coral samples. However, it should be mentioned that Esat and Yokoyama (2010) argued that the apparent open-system behavior could be explained by small variations of $^{234}\text{U}/^{238}\text{U}$ in seawater over the past 150 kyr.

Several other applications have been developed to date authigenic minerals (see Table 2), including the use of gypsum (Sanna et al. 2010) (Figs. 3 and 4). The methodology is similar to those used to date carbonates, but the lower U concentrations and greater difficulty dissolving

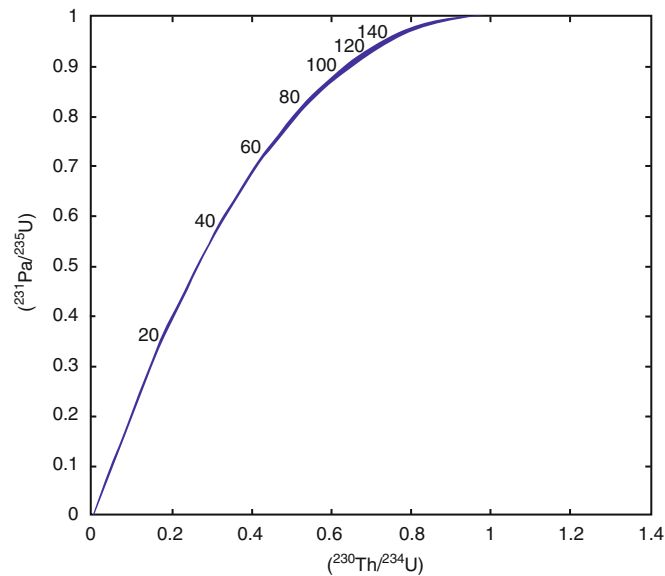


Fig. 4 Principle of concordia dating with the ^{230}Th – ^{234}U and ^{231}Pa – ^{235}U systems for authigenic minerals such as carbonates. Compositions that plot along the *curved line* are assumed to form with initial abundances of $^{230}\text{Th} = ^{231}\text{Pa} = 0$ and evolved subsequently toward secular equilibrium at isotope ratios of unity. The *curves* are labeled with ages in kyr

gypsum may limit its geochronological applications. One should mention also an extensive literature about the ^{230}Th – ^{238}U and ^{231}Pa – ^{235}U dating of apatite that can be applied to bones and teeth (see review by Grün et al. 2010).

Dating Detrital Carbonates

In the case of carbonates containing a detrital component, there is usually some Th incorporated at the time of formation, which means that one can no longer use Eq. 7 that assumes that the carbonate is initially Th-free. In cases where Th contents are substantial, the only reliable dating method is to apply an isochron technique to a series of co-genetic samples in a manner similar to the method used for dating volcanic rocks. To obtain a reliable date, one needs to make the assumption that all the carbonate subsamples formed at the same time, t , and were characterized by a constant $^{230}\text{Th}/^{232}\text{Th}$ ratio. However, the method requires that the co-genetic samples have variable $^{238}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ depending on the relative proportions of authigenic and detrital components in the form of a simple two-component mixture (Luo and Ku 1991; Bischoff and Fitzpatrick 1991; Ludwig and Titterton 1994). Luo and Ku (1991) have designed a method that allows the composition of the authigenic component to be determined. In this context, it can be shown that:

$$\left(\frac{^{230}\text{Th}}{^{232}\text{Th}}\right) = A \times \left(\frac{^{234}\text{U}}{^{232}\text{Th}}\right) + B \quad (9)$$

where

$$A = \left(\frac{{}^{230}\text{Th}^*}{{}^{234}\text{U}} \right)_a$$

$$B = \left(\frac{{}^{230}\text{Th}}{{}^{232}\text{Th}} \right)_0 e^{-\lambda_0 t} + \left[\left(\frac{{}^{230}\text{Th}^*}{{}^{234}\text{U}} \right)_d - \left(\frac{{}^{230}\text{Th}^*}{{}^{234}\text{U}} \right)_a \right] \times \left(\frac{{}^{234}\text{U}}{{}^{232}\text{Th}} \right)_d$$

where the subscripts *a* and *d* designate the authigenic and detrital component, respectively, and ${}^{230}\text{Th}^*$ represents the activity due to in situ decay of the authigenic or detrital component (subscripts *a* and *d*). Thus, by plotting $({}^{230}\text{Th}/{}^{232}\text{Th})$ versus $({}^{234}\text{U}/{}^{232}\text{Th})$, one can obtain the value of *A* and derive directly an age using the equation used for authigenic samples (Luo and Ku 1991). This method has proven useful in some cases but depends on the assumption of constant initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ for all the samples considered for the isochron. It has proven more reliable using total sample dissolution rather than leaching methods so that fractionation of Th and U caused by laboratory artifacts is avoided.

Dating Young Sediments

For dating young sediments, a commonly used approach is the ${}^{210}\text{Pb}$ dating method (Appleby and Oldfield 1978). In the oceans, ${}^{210}\text{Pb}$ is produced by the decay of ${}^{226}\text{Ra}$ within the ${}^{238}\text{U}$ decay chain. Furthermore, Pb is less soluble than Ra and is particle reactive. As a consequence, ${}^{210}\text{Pb}$ adsorbs onto sinking particles and shows an excess relative to values expected from the ${}^{226}\text{Ra}$ that is present in young sediments. The excess ${}^{210}\text{Pb}$ decays away as sediments age at a rate depending on the half-life of ${}^{210}\text{Pb}$ (22 years). Therefore, all of the excess of ${}^{210}\text{Pb}$ decays in about 100 years, which is the approximate range of this dating method. This method can be applied both to lake or ocean sediments.

Emerging Applications of U-Series Dating

Over the past few decades, thanks to analytical improvements, there has been a flurry of new applications of U-series dating methods both for low-temperature and high-temperature geological processes. Most of these applications have taken advantage of new possibilities afforded by modern analytical methods, using either smaller sample sizes, better precisions, or the possibility of in situ analyses. The sections below present some of these applications without attempts to be totally exhaustive.

Dating Surface and Subsurface Processes

By examining the fractionation between U, Th, and Ra in products of weathering in rivers and soils, it is possible to determine a timescale of chemical weathering or an age for the inception of weathering. Alternatively, it is possible in some cases to directly date the formation of authigenic phases formed as a result of secondary reactions. As recently reviewed in Chabaux et al. (2003), Chabaux et al. (2008), and Vigier and Bourdon (2011) and following the early work of Rosholt et al. (1966), Rosholt (1983), and Latham and Schwarz (1987) on soils, it is possible to calculate an age of weathering using simple kinetic models for the removal of ${}^{238}\text{U}$ relative to ${}^{230}\text{Th}$ or the removal of ${}^{234}\text{U}$ relative to ${}^{238}\text{U}$. By combining a kinetic model with mass balance considerations (Vigier et al. 2001; Dequincey et al. 2002), there are enough equations relative to unknown parameters such that an age can be calculated. This approach has been shown to be imperfect, but a comparison with other methodologies, such as those based on ${}^{10}\text{Be}$, has shown that these ages

provide good estimates of the timescale involved (Dosseto et al. 2008b). The basic equations that have been developed are as follows:

$$\frac{d^{238}\text{U}}{dt} = -k_8^{238}\text{U}_s \quad (10)$$

$$\frac{d^{234}\text{U}_s}{dt} = \lambda_8^{238}\text{U}_s - (k_4 + \lambda_4)^{234}\text{U}_s \quad (11)$$

where $^{238}\text{U}_s$ and $^{234}\text{U}_s$ represent a number of moles of ^{234}U and ^{238}U present in the solid phase, λ_4 and λ_8 are the decay constants for ^{234}U and ^{238}U , respectively, and k_4 and k_8 are the rates of release of ^{234}U and ^{238}U , respectively. A similar equation can be written for ^{230}Th in the solid. If both data for the solid phase and the aqueous phase are available, one can derive an age by solving these equations iteratively. An additional degree of complexity was introduced by Ghaleb et al. (1990) who used the following equation:

$$\begin{aligned} \frac{d^{238}\text{U}_s}{dt} &= -k_8^{238}\text{U}_s + F_8 \\ \frac{d^{234}\text{U}_s}{dt} &= \lambda_8^{238}\text{U}_s - (k_4 + \lambda_4)^{234}\text{U}_s + F_4 \end{aligned} \quad (12)$$

where F_8 and F_4 represent an input flux of ^{234}U and ^{238}U , respectively. Also, it is possible to use these equations to obtain a timescale of weathering provided some assumptions are made.

Dating of Pedogenic Cements and Hydrogenic Materials

The dating of pedogenic minerals uses an “isochron” approach that is different from the classical method used for volcanic rocks: a series of subsamples are assumed to be co-genetic and represent a binary mixture of authigenic cement, containing no ^{232}Th , and a fraction of detrital component that contains ^{232}Th . Each subsample is then assumed to evolve as a closed system. A modified isochron method was initially developed by Bischoff and Fitzpatrick (1991) and Ludwig and Tinterington (1994) when a detrital component is present (see section [Dating Authigenic or Biogenic Minerals](#)). The basic assumption is that $^{232}\text{Th}/^{238}\text{U}$ – $^{230}\text{Th}/^{238}\text{U}$ – $^{234}\text{U}/^{238}\text{U}$ data from a series of co-genetic samples containing variable amounts of a homogeneous detrital fraction can be used to obtain the $^{230}\text{Th}/^{234}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios of the detritus-free fraction, which can then be used to extract a meaningful age following the classical method of age determination in a Th-free carbonate. As argued by Candy et al. (2005), a careful sample selection and characterization is required to obtain coeval samples (immature calcrete) because mature calcretes tend to form over long timescales. In the study of Sharp et al. (2003) and Candy et al. (2005), the dating of pedogenic carbonates was used to study the evolution of alluvial terraces. Sharp et al. (2003) used carbonate rinds formed at the surface of clasts and by correcting for the contribution of a detrital component, were able to determine an “age” stratigraphy within individual rinds. A recent study of Neymark (2011) on calcretes has shown that the effect of recoil loss using the formalism of Thompson et al. (2003) (see section [Dating Authigenic or Biogenic Minerals](#) for details) required significant correction for calcretes older than 250 ka.

The development of laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) (Bernal et al. 2006 and see above) has enabled great advances in U-series dating methods that were inspired by the early work of Short et al. (1989). Short et al. (1989) showed it was

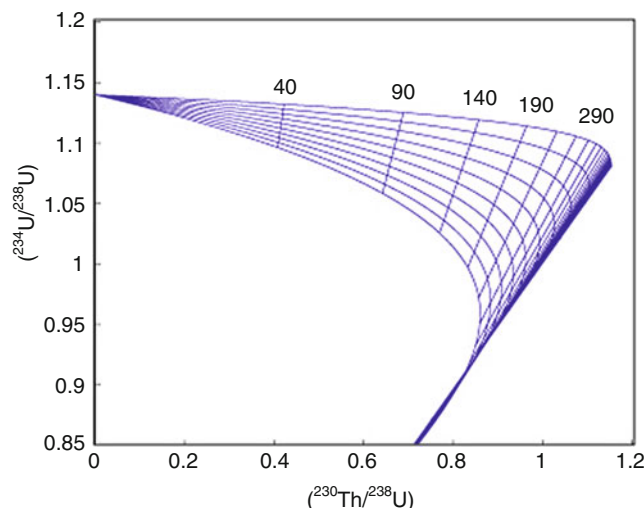


Fig. 5 Diagram illustrating the possibility of dating an open system with the ^{238}U – ^{234}U – ^{230}Th system according to the formalism of Thompson et al. (2003). This approach assumes that daughter nuclides can be redistributed within a mineral due to the effect of recoil ejection. In this context, it can be shown that isochronous samples should fall on a subvertical line anchored on the closed-system point. Thus the measurements of several such samples can yield an age. The subvertical lines correspond to points of equal age (labels are given in kyr)

possible to date Fe/Mn oxy-hydroxides with U–Th disequilibrium assuming the oxides formed with no initial Th. However, samples usually include a detrital component that requires correction prior to age calculation. One method for extracting age information from these materials is to plot $^{238}\text{U}/^{232}\text{Th}$ versus $^{234}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ versus $^{230}\text{Th}/^{232}\text{Th}$, where the slopes in these diagrams represent the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ values, respectively, of the detrital-free component (as described in section [Dating Authigenic or Biogenic Minerals](#)). It should be noted that in the Short et al. study, the two components were separated by leaching, a method that has been argued to be troublesome (Candy et al. 2005).

Using such an approach, it was possible for Bernal et al. (2006) to date Fe oxy-hydroxides using LA-MC-ICP-MS techniques. It should be noted that the soils in the study of Bernal et al. (2006) were developed on a U-rich protolith and thus the secondary hydroxides that formed were enriched in uranium (approximately 100 ppm) relative to common soils. The principle used for dating was based on the assumption that there is initially no ^{230}Th present in the pedogenic Fe oxy-hydroxides and that all ^{230}Th grew in situ with time. The data generally shows that rinds of nodules yield younger ages than their cores, as expected. The typical uncertainties obtained on the measured $^{230}\text{Th}/^{238}\text{U}$ ratios are on the order of 2–4 % (internal error), but the variability of the measurements along a depth profile suggests that the actual uncertainties might be larger.

A similar type of application was employed to date hyalitic opal using ^{238}U – ^{234}U – ^{230}Th disequilibrium, via in situ analysis by microdigestion or ion microprobe (Paces et al. 2004) (Fig. 5). As the opal was relatively rich in U and poor in Th, it was possible to date the micro-laminated material with the same method as that described for biogenic carbonates. Paces et al. (2010) were able to obtain ages that correlated with the microstratigraphic depths of sampling, indicating a well-behaved closed system. In some cases, this method can be coupled with U–Pb dating to extend dating to older ages (Neymark and Amelin 2008).

Dating of Weathering Rinds

Weathering rinds represent specific textures observed at the surface of clasts undergoing weathering, and many studies have focused on understanding how they formed and on establishing the rates of formation of these structures. U-series disequilibria offer an additional dating option because the formation of the rinds has been shown to be associated with an uptake of uranium (and no uptake or loss of Th) and because the rind may subsequently behave as a closed system. One can use the following equation to obtain an age:

$$\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_t = 1 + \left[\left(\frac{^{230}\text{Th}}{^{238}\text{U}}\right)_0 - 1\right]e^{-\lambda_0 t} + \frac{\lambda_0}{\lambda_0 - \lambda_4} \left[\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_t - 1\right] \left(1 - e^{(\lambda_4 - \lambda_0)t}\right) \quad (13)$$

Equation 13 is essentially similar to Eq. 7 except that it takes into account a nonzero initial abundance of ^{230}Th . This means that weathering rinds can be dated and the study of Pelt et al. (2008) has shown that it is even possible to obtain a depth profile with older ages at the outer parts of the rinds while zero ages are found at the basalt/weathering rind transition. Dating results showed a thickening of the rind with time and allowed a determination of a rate of rind formation. Furthermore, this rate is in agreement with a mass balance approach using major element chemistry and experimental data (Sak et al. 2010; Navarre-Sitchler et al. 2011). A second study by Ma et al. (2012) confirmed these earlier findings and suggested that the rate of rind formation is sensitive to the curvature of the starting material, as expected from numerical models by Sak et al. (2010).

Sediment Production: Comminution Ages

The production of sediments is accompanied by a breakdown of solid rocks into particles. The particles can be characterized by a size distribution, and it has been shown that much of the original rock mass may end up as fine-grained material. If the particles are small enough relative to the

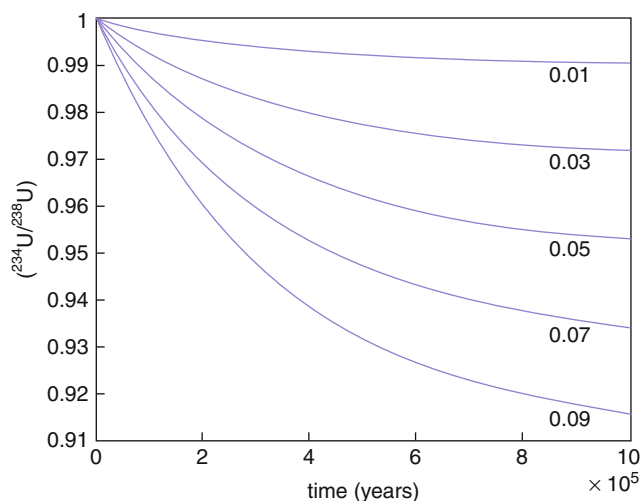


Fig. 6 Principle used for dating sediment production and transport using the comminution age model developed by DePaolo et al. (2006). In small enough particles, the energy imparted to the daughter nuclide of ^{238}U (^{234}Th) is sufficient to eject a fraction of the daughter nuclides (f_α) out of the particle. This ultimately leads to a deficit of ^{234}U in the solid particle that increases over time and can be used to obtain a date. The various curves were drawn for different values of f_α that are labeled accordingly

distance of recoil of ^{234}Th in silicate minerals (approximately 30 μm), then a sizeable fraction of recoiled ^{234}Th can be ejected out of mineral grains, provided the parent nuclide was located close enough to the edge. This concept has been utilized by DePaolo et al. (2006) to derive an age of sediment production that was termed “comminution age” (Fig. 6). Once the grains have reached their final size, it takes about five to six half-lives of ^{234}U (248 kyr) for the system to reach secular equilibrium. The differential equation describing the evolution of the system is:

$$\frac{d^{234}\text{U}_s}{dt} = \lambda_8^{238}\text{U}_s - \lambda_8 f_\alpha^{238}\text{U}_s - \lambda_4^{234}\text{U}_s \quad (14)$$

where f_α represents the fraction of ^{238}U lost by recoil. This is equivalent to having a smaller decay constant for ^{238}U . Starting from a grain at secular equilibrium, this leads to a deficit in ^{234}U which will eventually reach a new state of secular equilibrium after five to six half-lives of ^{234}U . The solution of this equation can be written as:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_s = \left(\left(\frac{^{234}\text{U}}{^{238}\text{U}}\right)_s^0 - (1 - f_\alpha)\right)e^{-\lambda_4 t} + (1 - f_\alpha) \quad (15)$$

There have been a number of attempts in the literature to derive meaningful ages using this method. Dosseto et al. (2010) showed that the variations in comminution ages were variable over climatic cycles in a given basin. The study of Lee et al. (2010) has shown that the ages obtained with this method were of the right order of magnitude and correlated well with an established stratigraphy using a totally independent geochronological method. However, resulting ages can differ, sometimes by up to a factor of two, which indicates that some issues need to be solved for this method to be fully applicable. First, one important aspect is to calculate the value of f_α , representing the fraction of ejected daughter nuclides. If the grains are assumed to be spherical, then the value of f_α can be calculated as:

$$f_\alpha = \frac{3\lambda_r L}{2d_p} \quad (16)$$

However, the surface of minerals is generally more complex, and it is possible to take the roughness of the surface into account to determine an effective value of f_α , as originally proposed by Semkov (1991) for calculating the emanation of radon:

$$f_\alpha = \frac{1}{4} \left[\frac{2^{D-1}}{4-D} \left[\frac{a}{R} \right]^{D-2} \right] R \cdot S_{BET} \rho_s \quad (17)$$

where D is the fractal dimension of the surface, a the diameter of the adsorbate molecule (N_2), R the recoil length, ρ_s the density of the solid, and S_{BET} the measured *BET* surface area. This approach was used by Bourdon et al. (2009) to study ^{234}Th recoil effects in a carbonate environment. This approach was further validated by Aciego et al. (2009) who demonstrated that if the value of f_α was calculated using Eq. 16, then the ^{234}U recoil ages of dust in ice core agreed with calibrated ages (see below). This result means that, at least for the mineral dust found in ice core, the conceptual approach is valid. This leads to a second potential issue with this method. In order to extract a representative value of the $^{234}\text{U}/^{238}\text{U}$ in the grains, the grains need chemical treatment to remove adsorbed uranium or secondary minerals formed at the surface. Unfortunately, this leaching may

lead to a laboratory fractionation of ^{234}U from ^{238}U and thereby artificially modify the calculated ages (Andersen et al. 2009; Hussain and Lal 1986). Handley et al. (2013) have examined the various sources of uncertainty and shown that the resulting uncertainty amounts to approximately 200 kyr. Clearly, this method is very promising but requires further development to fully understand natural versus laboratory effects.

Sediment Transport Time

In large river basins, the transport of sediments from the source (i.e., soils) to the oceans can last over timescales that are comparable with the half-life of U-series nuclides. In addition to the method proposed by DePaolo et al. (2006) that relies on ^{234}U – ^{238}U fractionation in small sediment particles, an additional method was first proposed by Dosseto et al. (2006b) based on a study of the Amazon basin. If the removal of uranium during sediment transport is sufficiently fast compared with the timescale of transport, one should observe an increase of $^{230}\text{Th}/^{238}\text{U}$ with time from sediment source to storage. Such a relationship was observed along the Amazon river, and using the formalism developed by Vigier et al. (2001), the transport time of the sediment could be estimated (see section [Dating Surface and Sub-Surface Processes](#)). Subsequent studies by Granet et al. (2007, 2010) have obtained similar results for Himalayan rivers, which suggest again that significant weathering takes place during transport. One potential caveat of this method is the effect of ^{230}Th adsorption onto particles during transport. However, Dosseto et al. (2006b) argued that this effect should be coupled with a decrease in $^{226}\text{Ra}/^{230}\text{Th}$ during transport, which was not observed. This approach was extended by Granet et al. (2010) to studies of different size fractions of sediments, and it was shown that the small grain size sediment travel faster than the coarser grain, as expected.

Dating Ice Cores

The basic concept for dating ice cores using U-series nuclides was introduced by Fireman (1986) and further developed by the work of Goldstein et al. (2004). The dust that is incorporated in ice contains uranium at sufficient levels such that recoil of ^{234}Th results in an accumulation of measurable amounts of ^{234}U in the ice phase over time. Thus, if one carefully melts the ice and separates the dust, it is possible to determine when the dust was trapped in the ice. The amount of ^{234}U accumulated in the ice depends on the amount of dust present in the ice, the concentrations of uranium in the dust, and time. The application of such a methodology has several important requirements: (1) a careful separation of liquid and solid phases that avoids adsorption of uranium onto the dust during the melting of the ice. This aspect was studied by Goldstein et al. (2004) who developed a method utilizing EDTA in a buffer solution, which provided an efficient separation, (2) an extremely careful evaluation of the processing blanks as large samples are needed, (3) excellent sensitivity for the mass spectrometric measurements due to the small amounts of ^{234}U recoiled in the ice (Aciego et al. 2009, 2011), and (4) an accurate determination of the efficiency of ^{234}Th recoil (f_α) into the ice from a given particle. The typical grain size of dust in ice core is approximately 1–2 μm , and as the dust is sorted by wind transport, the grain size distribution is relatively narrow. As explained in section [Dating of Weathering Rinds](#), the recoil efficiency (f_α) is a parameter that needs to be determined quantitatively in order for the dating method to be functional. Aciego et al. (2011) applied the approach of Semkow (1991) to determine f_α for dust in ice core using a specifically designed device to measure BET surface area in small-sized samples (a few mg). Aciego et al. (2011) analyzed a series of samples from the Dome C ice core in Antarctica and found that by measuring the accumulated ^{234}U in the ice, a precise age could be determined. The resulting U-series ages matched those determined independently using the calibrated age-versus-depth curve established by Parrenin et al. (2007).

Dating of Magma Storage

There have been two main avenues of development for determining the ages of phenocrysts and the timescale of magma storage using U-series methods. First, the analysis of accessory minerals with either in situ methods or with fine-scale sampling makes it possible to directly estimate crystallization ages. Second, by comparing analyses of $^{226}\text{Ra}/^{230}\text{Th}$ in minerals with that of the melt in equilibrium, it is possible to estimate the timescale of magma crystallization.

Dating of Accessory Minerals

The relatively high concentrations of U and Th in accessory minerals such as zircon, monazite, xenotime, and apatite make them an obvious target to determine ages of crystallization in magmatic systems. Among these, zircon has been shown to have remarkable properties for geochronology for the U–Pb system, and it was a logical extension to use it with U-series disequilibria. A specific advantage of zircon is that the U–Th partitioning in zircon relative to the melt yields a large fractionation (Blundy and Wood 2003) making this mineral ideally suited for dating. Using a single analysis of zircon together with a whole-rock analysis, one can derive an age using a “two-point” isochron approach. For example, Charlier et al. (2005) were able to determine ages of zircons by separately analyzing the cores and rims of zircon in the Taupo volcanic zone using MC-ICP-MS. Results showed a protracted history of crystallization of more than 90 ka that was not revealed by whole-rock analysis. In a second, more extensive study of the Taupo volcanic zone, Charlier and Wilson (2010) were able to obtain a wide age distribution of zircons in various eruption centers and showed that large volcanic complexes involve recycling and assimilation of older crystal mush. These geochronological data can be coupled with trace element analyses so as to obtain an integrated time history of the chemical evolution of a volcanic system (e.g., Klemetti et al. 2011). More recently, Schmitt (2006) analyzed zircon from the Laacher See volcanics and was able to show that these minerals formed late in the crystallization sequence. In contrast, Schmitt et al. (2010) used secondary-ion mass spectrometry (SIMS) to analyze U–Th disequilibria in pyrochlore found in carbonatites from the same volcanic system and obtained U–Th isochrons that showed that the lifetime of the magma chamber was approximately 10–20 ka, in agreement with an earlier study by Bourdon et al. (1994).

$^{226}\text{Ra}/^{230}\text{Th}$ Dating of Phenocrysts and Magma Storage Times

Initial attempts to use ^{226}Ra – ^{230}Th disequilibrium to date volcanic events were based on the idea that because ^{226}Ra had no stable isotope, one could use Ba as its chemical analog, and a Ra/Ba dating technique similar to Th–U dating (see section [Dating Volcanic Rocks](#)) was proposed (Rubin and Macdougall 1990; Volpe and Goldstein 1993). For young volcanic systems, this method yielded ages that were significantly older than the age of eruptions, but it was unclear to what extent the age determinations were reliable. Since then, Ra and Ba partitioning data has been determined experimentally (rather than theoretically as in Blundy and Wood 2003), and it is now known that Ba and Ra have distinct partition coefficients in minerals that incorporate those elements (Fabbrizio et al. 2009).

In parallel, a method for direct dating of plagioclase phenocrysts was developed by Cooper et al. (2001) (Fig. 7). This method yields timescales of plagioclase crystallization assuming that the mineral had grown in equilibrium with the melt and that it evolved in a closed system since then. By comparing the measured $^{226}\text{Ra}/\text{Ba}$ ratios in plagioclase with values expected using predicted partition coefficients for Ba and Ra between plagioclase and melt, it is possible to determine the time that must have elapsed since crystallization. Stelten and Cooper (2012) used a combination of Ra/Ba dating of plagioclase and U–Th disequilibrium dating of zircons in the same rhyolitic system

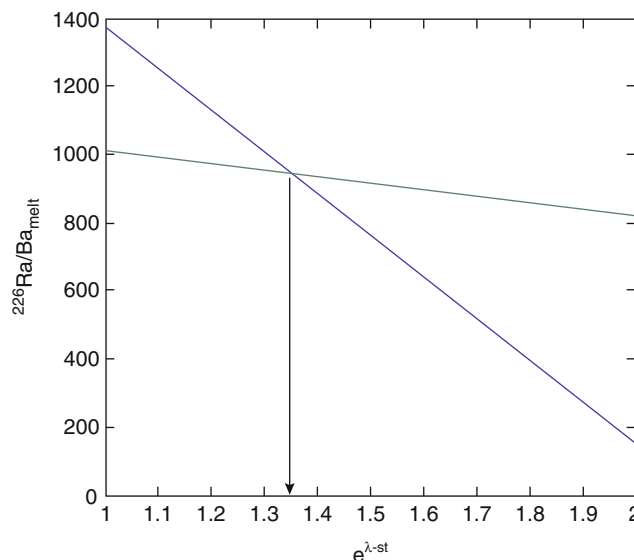


Fig. 7 Illustration of the ^{226}Ra –Ba dating of plagioclase phenocrysts developed by Cooper et al. (2001). The plagioclase is assumed to have formed in chemical equilibrium with the magma having an initial $(^{226}\text{Ra}/\text{Ba}_0)$. The magma and plagioclase then evolve as closed system until time t . The negatively sloped lines represent the values of $(^{226}\text{Ra}/\text{Ba})$ measured in the melt (*blue*) and the values of $(^{226}\text{Ra}/\text{Ba})$ calculated for the melt based on the plagioclase (*green*) as a function of $e^{\lambda_{\text{st}}}$. The intersection corresponds to the time when the plagioclase formed

to demonstrate the existence of distinct magmatic pools with both old and young ages. Their study also illustrated that the dating of phenocrysts is not straightforward in long-lived systems. There have been refinements of this method since then (Cooper and Reid 2003, 2008), and it is now more clear what requirements are needed, given that in some cases, the ages were not what was expected. The study of Sims et al. (2013) on phenocrysts from Mount Erebus volcano in Antarctica has shown that this method was sensitive to the degree of magma replenishment in a magma chamber and that the data could be better interpreted assuming an open magmatic system.

Another method that has been developed in parallel is the dating of magma storage time based on Ra–Th systematics in whole rocks. The study of Vigier et al. (1999) on the Ardoukoba eruption in the Asal rift, Djibouti, has shown that over the same eruption, different pools of magmas were erupted. Furthermore, these magmas showed a negative correlation of Ra/Th with Th indicating that the most differentiated magmas had lower Ra excesses. This could not be explained by assimilation of older magmas or by plagioclase crystallization. This approach was extended to other magmatic systems by Blake and Rogers (2005). Studies by Yokoyama et al. (2006) and Chekol et al. (2011) have shown that ^{226}Ra – ^{230}Th systematics were sometimes affected by crustal assimilation and that simple radioactive decay is not always sufficient to describe the evolution of ^{226}Ra in the melt.

Summary

Radioactive disequilibrium in the uranium decay series (either ^{238}U or ^{235}U) is caused by fractionation processes that can occur between isotopes within the chain based on differences in their nuclear or chemical properties. Because the intermediate daughter products are themselves radioactive, the U-series nuclides will tend to return to a state of secular equilibrium at rates that depend on the decay constants of each isotope. As a result, a number of geochronometers have been developed that can be used to date a wide variety of materials at timescales ranging from decades to over a million years.

These methods have been devised to date near-surface processes including deposition of authigenic and biogenic precipitates, development of soils, rates of rock weathering and rates of mineral comminution, deposition of young sediments, and sediment transport times, as well as processes occurring at depth within the crust and mantle including dating of young volcanic rocks or dating of crystal residence times in magma chambers. Emerging studies have taken advantage of advances in analytical capabilities that allowed analysis of low-level samples with greater precision or higher spatial resolution. The field of U-series dating has now become a mature technique for dating Quaternary geological or archeological materials of increasing diversity.

Cross-References

- ▶ [²¹⁰Pb Dating](#)
- ▶ [Alpha Spectroscopy](#)
- ▶ [Bones, \(U-Series\)](#)
- ▶ [Carbonates, Lacustrine \(U-Series\)](#)
- ▶ [Carbonates, Marine Carbonates, \(U-Series\)](#)
- ▶ [Carbonates, Speleothem Archaeological, \(U-Series\)](#)
- ▶ [Carbonates, Speleothem Climatic, \(U-Series\)](#)
- ▶ [Chemical Weathering \(U-Series\)](#)
- ▶ [Faults \(U-Series\)](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Secondary Ion Mass Spectrometer \(SIMS\)](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [Uranium Series, Ice](#)
- ▶ [Uranium Series, Opal](#)
- ▶ [Uranium Series, Volcanic Rocks](#)
- ▶ [Uranium–Lead Dating](#)
- ▶ [Uranium–Lead Dating, Opal](#)
- ▶ [Uranium–Lead, Zircon](#)

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Aquifer Characteristics (U-Series)

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Definition

Groundwater concentrations of naturally occurring isotopes in the ^{238}U , ^{235}U , and ^{232}Th decay series that are used to identify and quantify a range of aquifer characteristics.

Essential Concepts

The radionuclides ^{238}U , ^{235}U , and ^{232}Th decay in a series of shorter-lived radionuclides, and these decay series (Fig. 1) provide an important tool for investigating various aquifer characteristics, including chemical parameters, flow patterns, and transport of actinides. The relationships between the radionuclides in groundwater provide the potential for readily quantifying parameters of water/rock interaction from direct measurements of waters alone, with trace element source terms and bulk adsorption coefficients inferred from comparison between the different radionuclides.

The point of comparison for groundwater radionuclides is the secular equilibrium generally occurring within minerals, in which the activities (the number of atoms times the decay constant) of all the radionuclides in a decay series are the same. When this is disrupted by an event or process that changes the relative proportions of the isotopes within a decay series, the activity of each isotope will evolve until it again reaches equilibrium with its parent isotope, over a time of several half-lives of the isotope itself. Within groundwaters, activities vary widely between the radionuclides (which are therefore in disequilibrium), as shown in Fig. 2, due to the contrasting chemical behavior of the elements involved. The highest activities are for ^{222}Rn , which, as a noble gas, does not react with the aquifer solids. The actinide U, which is soluble in oxidizing waters, is often present in intermediate activities that are moderated by removal onto aquifer rocks by adsorption and, in some cases, precipitation. The alkaline earth element Ra and the actinide Th are strongly depleted due to water/rock interactions. Both of these elements have very short-lived as well as longer-lived isotopes, and so their isotope compositions reflect processes occurring over a range of timescales. The concentration of each isotope is also controlled by the rate at which it is supplied. Ongoing processes that maintain a steady-state supply of each isotope will maintain disequilibrium between parent and daughter isotopes; however, when there are changes in hydrodynamic conditions, activity concentrations will adjust to the new steady-state supply over a time of several half-lives of the daughter isotope. Overall, since the isotopes in each decay series are tied to one another by decay systematics, with daughter nuclide productions and distributions dependent upon parent distributions, combined studies of the elements in these series can generate considerable information regarding radionuclide water/rock interactions.

It is generally difficult to quantify aquifer parameters that control trace element behavior by direct measurements. Host rocks typically cannot be as readily sampled as groundwater, and average values for rocks recovered from boreholes are difficult to obtain. Some of this information has been

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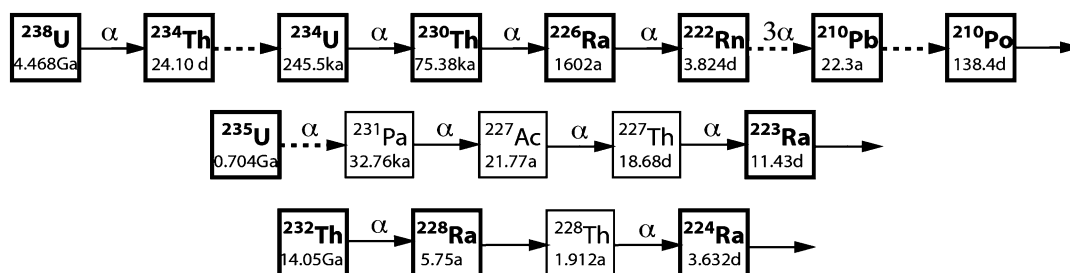


Fig. 1 The isotopes of the ^{238}U , ^{235}U , and ^{232}Th decay series. The isotopes in *bold* are those most commonly measured in groundwater studies. The *dashed arrows* indicate where isotopes have been *left out* that have very short half-lives and so are measured only in rare cases. Radioactive half-lives are given below each isotope in units of billions of years (Ga), thousands of years (ka), years (a), or days (d)

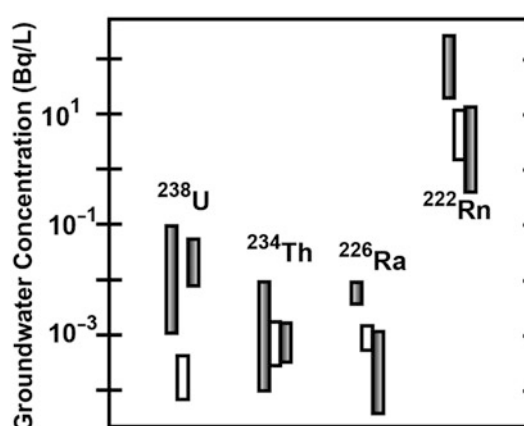


Fig. 2 The ranges of activity concentrations (in becquerels per liter or decays per second per liter) measured in three aquifers are shown side by side for select isotopes in the ^{238}U decay series (after Porcelli 2008). There are wide variations for each isotope reflecting site conditions and between isotopes reflecting the different chemistries of the elements

sought from aquifer tests using experimentally introduced tracers and from laboratory experiments on aquifer materials, but these studies are labor intensive and necessarily limited in scale of both time and space. Measurement of radioactive decay series isotopes allows a number of aquifer characteristics to be investigated including mixing of groundwater into marine and surface water reservoirs, tracking of groundwater flow, estimating radionuclide migration rates, determining recent precipitation, locating redox boundaries within an aquifer, and dating groundwater within an aquifer.

The Supply of Radon and Other Radionuclides by Recoil

As shown in Fig. 1, some radionuclides are produced by high-energy α decay, while some are produced by low-energy β decay. In the former, decay is sufficiently energetic that during decay, the daughter isotope is propelled $\sim 100 \text{ \AA}$ (10^{-8} m) through the mineral in which it was produced, possibly resulting in expulsion from the mineral. It is a physical process, in contrast to the chemical processes affecting the radionuclides involved. Short-lived nuclides in groundwater are supplied primarily by this mechanism as well as by decay of dissolved and adsorbed parent isotopes. The recoil rate is therefore a key parameter. For long-lived nuclides in the decay series, weathering of U- and Th-bearing minerals may also be significant.

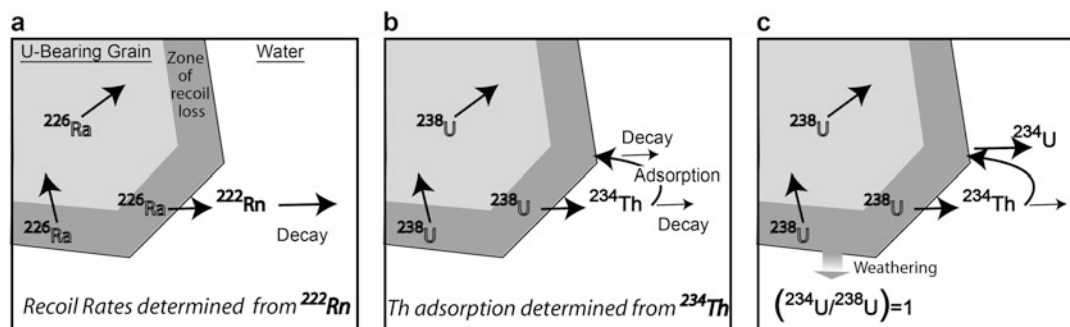


Fig. 3 Recoil rates of nuclides in the ^{238}U decay series are determined from ^{222}Rn concentrations. Applied to ^{234}Th , the extent of adsorption of Th can be calculated. The isotope ^{234}U is supplied by both recoil and weathering, which leads to $^{234}\text{U}/^{238}\text{U}$ activity ratios (designated as $^{234}\text{U}/^{238}\text{U}$) in groundwater of greater than 1

The radionuclide that is simplest to understand is ^{222}Rn (Fig. 3). Since Rn is an unreactive noble gas, groundwater ^{222}Rn is entirely dissolved, and this can be directly measured in waters pumped to the surface. It is removed only by decay and not by adsorption or precipitation. The main supply is from recoil caused by α decay of ^{226}Ra that is contained in minerals with ^{238}U . The recoil rate is simply equal to the rate at which ^{222}Rn is removed by decay. Therefore, the recoil rate can be determined simply from the rate of decay of dissolved ^{222}Rn , and this can then be used to determine the recoil rate of other nuclides.

The fraction of the total ^{222}Rn produced in the aquifer solids that is supplied to groundwater through recoil is dependent upon the size of the ^{226}Ra -bearing grains, with small grains having a larger proportion of the contained ^{226}Ra within recoil distance of grain surfaces. Measured ^{222}Rn groundwater activities have been obtained that correspond to as much as ~10 % of the total amount produced in the aquifer rock. Where the proportion of recoil ^{222}Rn in groundwater is this large, parental ^{226}Ra is typically interpreted to reside in very small mineral grains or in secondary surface coatings.

Adsorption of Ra, Th, and U

Another important parameter determining element behavior in an aquifer is the bulk adsorption coefficient, which is the ratio of atoms adsorbed onto surfaces to the atoms in solution. This is approximately equal to the retardation factor, which is the ratio of the rate of groundwater flow to the rate of element migration. Therefore, elements with a high partition coefficient, and so high retardation factor, migrate correspondingly slower. This parameter can be determined for each isotope from the rate of recoil and its groundwater concentration and so can provide overall rates of transport of Ra, Th, and U as well as of water/rock interaction processes affecting these elements. This is regardless of the actual mechanisms involved, and so the information complements small-scale physical chemistry studies that can identify the controlling processes.

The case for ^{234}Th is shown in Fig. 2b. When the ^{234}Th concentrations dissolved in groundwater and adsorbed on mineral surfaces are in steady state, the input from recoil is equal to the removal rate by decay in solution and on the surfaces. If the recoil rate is known from the concentration of ^{222}Rn , then the adsorption coefficient of ^{234}Th , and so of the element Th, can be determined. Similarly, the adsorption coefficients of Ra, Po, Pb, and U can also be determined. It should be noted that the supply of any daughter nuclide is dependent not only upon recoil from parent atoms within primary minerals but also by removal onto adsorption sites and incorporation into secondary minerals.

Precise calculations therefore are somewhat more complex, since weathering, recoil, adsorption, and precipitation have affected the distribution of the parent isotope in the decay series, which in turn is dependent upon the effects of parent isotopes further up the decay chain. Mathematical treatments of simple aquifer models can be found in Krishnaswami et al. (1982), Ku et al. (1992), and Porcelli (2008).

Using these methods, the Ra partition coefficients in various freshwater aquifers have been determined to be in the range of 10^3 – 10^4 . In saline aquifers, the adsorption of Ra drops substantially due to competition for adsorption sites. In freshwater aquifers, Th is generally adsorbed 10^1 – 10^2 times more efficiently than Ra. Values for U in the same aquifers of $\sim 10^3$ have been found, though elsewhere there is evidence for much lower adsorption (see Porcelli 2008). Values for Po vary as much as 10^1 – 10^6 , and Pb has been found to have values of 10^{-2} – 10^1 times those of Po (Porcelli 2014).

Interpreting U Isotope Compositions

The ($^{234}\text{U}/^{238}\text{U}$) ratio (the ratio of activities of the two isotopes, as denoted by the parentheses) can provide useful information on aquifer characteristics and serve as a groundwater tracer. While the concentrations of ^{238}U in groundwaters are controlled by weathering (like other, stable trace elements), which generally releases U with ($^{234}\text{U}/^{238}\text{U}$) = 1, the concentration of ^{234}U is controlled by both weathering and recoil (Fig. 3). The decay of ^{238}U produces ^{234}Th , which can be recoiled out of mineral grains and which then produces ^{234}U by low-energy β decay. The ($^{234}\text{U}/^{238}\text{U}$) ratio therefore reflects the ratio of the rate of recoil to the rate of weathering. The recoil flux is generally simply proportional to the surface area and U concentration of U-bearing grains. The weathering rate is controlled by the composition of the host grains and groundwater chemistry. It is also proportional to the surface area and U concentration.

A number of aquifer conditions will have predictable effects on the ($^{234}\text{U}/^{238}\text{U}$) ratio and U concentration of groundwater. Differences in the minerals that contain U will affect both ($^{234}\text{U}/^{238}\text{U}$) ratios and U concentrations, since it will change the rate at which U is released by weathering. Similarly, changes in groundwater chemistry can change the weathering rate of minerals. Differences in the U precipitation rate will result in different U concentrations, but not in different ($^{234}\text{U}/^{238}\text{U}$) ratios. Differences in the adsorption coefficient of U, e.g., due to changes in pH or the presence of adsorbing minerals, will have no effect on the U isotope composition. Differences in the surface area of U-bearing minerals, e.g., by differences in average grain size or in the abundances of U-bearing minerals, will affect recoil and weathering of U equally and so will not change the ($^{234}\text{U}/^{238}\text{U}$) ratio of the water.

Applications

The systematics of isotopes within the U and Th decay series provide a range of tools, useful over different timescales, which can be used to trace groundwater, identify aquifer processes, and quantify water/rock interactions. Examples include:

Determining marine groundwater discharge. There can be significant discharge of groundwater offshore and into shallow coastal waters, and this can be identified with Ra isotopes. Saline coastal groundwaters are enriched in the long-lived ^{226}Ra and especially ^{228}Ra compared to seawater. The

short-lived ^{223}Ra and ^{224}Ra isotopes are also enriched in saline and fresh groundwaters and highly depleted in seawater. Assuming that the concentrations in coastal waters are in steady state, from estimates of the water residence time, the influx of groundwater-derived Ra, and so groundwater fluxes, can be determined. The ($^{228}\text{Ra}/^{226}\text{Ra}$) ratio can also be used to identify groundwater sources, since younger groundwaters, or aquifers recently flushed by saline water intrusion, have higher ratios since it takes longer for ^{226}Ra concentrations to build up outside minerals. Short-lived ^{222}Rn can also be used to evaluate very recent groundwater inputs. These methods have been used to successfully map groundwater discharge across large coastal areas (Charette et al. 2008).

Tracking groundwater flow. In freshwater systems, U isotopes may be used to trace groundwater flow and mixing, while Ra and Th are too strongly adsorbed to be useful as water tracers. Aquifers with different characteristics may generate different groundwater ($^{234}\text{U}/^{238}\text{U}$) ratios that can serve as fingerprints and so can be used in hydrologic studies to identify mixing and flow patterns. For example, older groundwaters in aquifers with low weathering rates may have higher ($^{234}\text{U}/^{238}\text{U}$) ratios than those in shallow aquifers so that the location and magnitude of fluxes into overlying waters can be identified. Similarly, where there are aquifers composed of very different rock types with different weathering release rates of U, ($^{234}\text{U}/^{238}\text{U}$) ratios can be used to trace groundwater mixing. This can include identifying higher velocity flow paths where waters enter an aquifer with distinctly different characteristics (Roback et al. 2001).

Identifying groundwater inputs to surface waters. Similarly, the contributions of waters from different groundwaters into lakes and rivers can be identified using ($^{234}\text{U}/^{238}\text{U}$) ratios, especially when coupled with other tracers such as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This can include the relative proportions of inputs from shallow and deep aquifers or from aquifers of different rock types and watersheds along a river (Riotte and Chabaux 1999).

Estimating pollutant radionuclide migration rates. Determination of the behavior of naturally occurring U and Th can be used to predict the mobility of released anthropogenic actinides and so can be part of site risk assessments for nuclear facilities. Naturally occurring nuclides are present in very low concentrations, so that the measured extent of adsorption cannot be directly extrapolated to pollutants with much higher concentrations and possibly accompanied by changes in aquifer chemistry. However, they still provide a baseline for establishing the relevant adsorption factors and may remain relevant for lower levels of contamination (Porcelli 2008).

Determining “recent” mineral precipitation. The nature of minerals precipitating within an aquifer reflects the chemical conditions of the groundwaters. While rocks within aquifers generally are composed of primary minerals having U and Th decay series nuclides within secular equilibrium, secondary minerals that incorporate radionuclides from groundwater will initially show substantial secular disequilibrium. The resulting ^{230}Th - ^{234}U - ^{238}U compositions can be used to date the hydrogenic minerals and so determine the timing and history of precipitation from migrating solutions.

Locating redox boundaries. Under reducing conditions, U forms relatively insoluble U^{4+} and precipitates as UO_2 . As groundwater moves past a redox boundary, groundwater U concentrations drop and the enhanced recoil rates from fine-grained U oxides increase the ($^{234}\text{U}/^{238}\text{U}$) ratio, providing a way for mapping aquifer redox fronts from U isotope distributions (Osmond and Cowart 2000).

Dating groundwaters. There have been various studies that used U isotopes for dating groundwaters. If the ^{238}U concentration along a flow line is constant or varies in a clearly defined way and the recoil input of ^{234}U is constant, then the ($^{234}\text{U}/^{238}\text{U}$) ratio evolves primarily by decay and can be used to determine the age of the groundwater (Ivanovich et al. 1991). However, such conditions rarely are evident. For shorter timescales, Ra might be used. In highly saline

groundwaters where Ra is not adsorbed and where the recoil inputs of Ra isotopes are constant, then the ^{228}Ra activity will increase over $\sim 20\text{a}$ until it reaches a steady state, and so can be used to date young waters (Kiro et al. 2013). In principle, the longer-lived isotope ^{226}Ra can be used for waters with ages up to $\sim 5\text{ ka}$.

Summary

Isotopes in the ^{238}U , ^{235}U , and ^{232}Th decay series chains provide numerous tools to study aquifer processes. With a wide range of half-lives, these isotopes can be used to investigate very rapid processes such as adsorption as well as longer-term processes from precipitation to basin-wide aquifer flow. The elements represented in the decay series also have a range of chemistries, providing investigative methods that are applicable to different aquifer aspects and conditions. This includes the strongly adsorbed elements Th, Pb, and Po, the relatively mobile U, and Ra, which is only strongly adsorbed in fresh waters. There are some fundamental aspects of radionuclide behavior that require further investigation, including the reversibility of adsorption, factors that may affect release from minerals by recoil or leaching, and the effect of colloids. Progress in these fields, as well as new aquifer studies, will undoubtedly lead to new methods for extracting information on aquifer characteristics from the decay series.

Cross-References

- [Aquifer Residence Time \(\$^{36}\text{Cl}\$ \)](#)
- [Chemical Weathering \(U-Series\)](#)
- [Uranium-Series, Opal](#)
- [U-Series Dating](#)

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Bones (U-Series)

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Synonyms

²³⁰Th/U dating of bone; U-series disequilibrium dating of bone; U–Th dating of bone

Definition

Uranium-series dating: A geochronological method that uses intermediate decay products in the ²³⁸U or ²³⁵U radioactive decay chains to measure the length of time required to reach the current state of radioactive disequilibrium from an initial condition.

Bone: A dense, semirigid, porous, calcified connective tissue forming the major portion of the skeleton of most vertebrates consisting of an organic matrix, largely collagen, and a mineral phase of nonstoichiometric carbonate hydroxyapatite Ca₁₀(PO₄)₆(OH)₂.

Introduction

Uranium-series disequilibrium dating of carbonate precipitates provides one of the most precise (and accurate) dating methods for the last 500 ka and has found application in archaeology for dating flowstone floors that cap or bracket archaeological deposits (e.g., Schwarcz and Blackwell 1992) or that are associated with cave paintings (Pike et al. 2012). The restricted range of contexts where suitable carbonate samples are associated with cultural layers, however, limits its applicability to archaeological chronology. Because of this, considerable effort has been made to attempt to apply the U-series method directly on archaeological bone.

Living bone is a composite of protein (largely collagen) and nonstoichiometric carbonate hydroxyapatite (often referred to as bioapatite). It contains only traces of uranium (<a few ppb), whereas archaeological bone can contain many 10 s of ppm. Unlike calcite flowstones, bone is an open system; it gains most of its uranium from the burial environment, and any attempt to calculate a U-series date from measurements of ²³⁴U, ²³⁸U, and ²³⁰Th requires the application of a model of this uptake.

The Early Uptake Assumption

Early attempts at U-series dating of bone simply treated it as an approximation to a closed system, using the “early uptake” (EU) assumption – that the uranium was taken up by the bone initially over a short period of time relative to its age. A comparison of radiocarbon dates (between 10 and 30 ka) with EU U-series dates on bones showed an overall average underestimation in the U-series dates of

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2,700 years and appeared initially to support the EU assumption (Szabo 1980). Given most of the bones were only slightly older than 10 ka, however, this is still a significant underestimation. While use of the EU assumption was widespread in early attempts to date bone, often with very mixed results (e.g., Szabo et al. 1973), a chemical or physical mechanism for it was not formally proposed until the work of Rae and Ivanovich (1986). It had previously been proposed (e.g., Szabo 1980) that the primary mechanism for incorporation of uranium in bone was by substitution for Ca^{2+} in the bone mineral hydroxyapatite. Because of differences in their ionic radii, this necessitated the reduction of U^{6+} to U^{4+} . In most burial environments, uranium is in the mobile U^{6+} (uranyl) rather than the immobile U^{4+} form (Gascoyne 1982), but Rae proposed that the conditions needed for reduction would be present in archaeological bone as a result of the decomposition of the bone's organic matrix – collagen – into its constituent amino acids. This mechanism would explain not only how the uranium was fixed in the bone through reduction to U^{4+} and substitution for Ca but also how uranium can be incorporated early in the burial history of a bone after which further uptake ceases. Collagen is rarely found in bones older than a few tens of thousands of years and almost never in bones older than 100 ka. Therefore, according to Rae's proposal, the uptake of uranium should be limited to the early stages of burial history of a bone – the period while the collagen is degrading. While this mechanism seemed plausible, Rae herself found dates calculated using the EU assumption to give mixed results, especially from open-air (non-cave) sites (Rae et al. 1989), and also noted that some bones appeared to give older than expected results, probably as a result of the loss of uranium unaccounted for in the EU model. The few further systematic studies comparing EU U-series dates with expected ages were unable to substantiate EU behavior as a general feature of bone (e.g., see Pike and Pettitt 2003).

Open-System Modeling Using $^{230}\text{Th}/\text{U}$ and $^{235}\text{U}/^{231}\text{Pa}$

In parallel, there were a number of attempts to model the open-system behavior of bone using combined $^{230}\text{Th}/\text{U}$ and $^{235}\text{U}/^{231}\text{Pa}$ measurements (e.g., Szabo and Malde 1969; Szabo et al. 1973; Szabo and Collins 1975; Szabo 1979). Lacking a geochemical model of uranium-bone interactions, these models were generally straightforward mathematical assumptions, albeit with plausible physical implications. For example, a model proposed by Szabo and Rosholt (1969) with later modifications by Chen and Yuan (1988) incorporated uranium uptake in two stages: an initial period of rapid uptake followed by a second later episode of either uptake or loss of uranium. Using isochronous samples (e.g., multiple bones from a single archaeological layer) that were assumed to have been affected by the second migration at the same time but to different extents, they calculated a corrected age from $^{230}\text{Th}/\text{U}$ and $^{235}\text{U}/^{231}\text{Pa}$ (see Cheng et al. 1998 for more on U/Pa systematics). While this method was used to provide chronologies for a number of key sites in China, which in turn raised the intriguing possibility of chronological overlap between *Homo erectus* and archaic *Homo sapiens* (Chen and Zhang 1991), subsequent redating of the sites with U-series and other techniques has shown the ages of the *H. erectus* sites to be much older than estimated by Cheng and Yuan's model (e.g., Grün et al. 1998; Shen et al. 2001; Zhao et al. 2001).

The Diffusion-Adsorption Model

A key development in the understanding of uranium uptake mechanisms in bone was the work of Millard and Hedges (1995, 1996). In contrast to Rae's explanation for EU which required

the reduction of U^{4+} to U^{6+} , in vitro experiments by Millard and Hedges found uptake of uranyl (i.e., U^{6+}) in protein-free hydroxyapatite and measured a partition coefficient between hydroxyapatite and uranyl solution of 10^4 – 10^6 , in agreement with estimations from observations on archaeological bone. Drawing on mathematical models of diffusion developed by Crank (1975), they proposed an explicit geochemical model of uranium uptake, the diffusion-adsorption (D-A) model, where diffusion was the dominant transport mechanism of uranyl ions into bone pores where it was subsequently adsorbed onto the large ($>100 \text{ m}^3 \text{ g}^{-1}$) surface area of bioapatite.

Using formulations given by Crank (1975), Millard and Hedges proposed the diffusion equation for simultaneous diffusion and adsorption as

$$\frac{\partial C}{\partial t} = \frac{D}{(R+1)} \frac{\partial^2 C}{\partial x^2}$$

where C is the uranium concentration at a point x in the bone, D is the diffusion coefficient reduced for diffusion in a porous medium such as bone, and R is the volumetric partition coefficient which is related to the partition coefficient (K_d) by $R = K_d/p$ where p is the specific porosity of the bone. Both D and R can be related to the physical structure of bone (e.g., volume, size distribution and tortuosity of bone pores, and the internal surface area).

Using a modification of Crank's equation for diffusion in an infinite planar slab and assuming a linear adsorption isotherm, they derive the concentration (ppm), Z , at a point x :

$$Z_{(x)} = pRC_1 \left(1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{\left[\frac{-D(2n+1)^2 \pi^2 t}{(R+1)4l^2} \right]} \cos \left[\frac{(2n+1)\pi x}{2l} \right] \right)$$

where x is the distance from the center of the slab (cm), t is the time of burial, C_1 is the environmental concentration of uranyl (ppm), and l is half the thickness of the bone (cm). To simplify this, Millard and Hedges use three reduced dimensionless parameters:

$$Z' = Z/pRC_1 \quad x' = (x-l)/l \quad t' = tD/(R+1)l^2$$

Under this scheme, Z' represents the fraction of the equilibrium concentration of uranium in the bone, since at equilibrium the concentration of uranium, Z , is pRC_1 . The parameter x' represents the fractional distance from the center of the bone section and takes a value of -1 to 1 . The parameter t' is a function of both time and D/R . Young bones or bones with lower D/R give smaller t' .

Not only can the D-A model predict the rate of accumulation of uranium in bone, but it also predicts the distribution ("profiles") of uranium and uranium-series isotopes transversely across a bone (Fig. 1). Under constant geochemical conditions, the model predicts the diffusion of uranium from the outer and inner (medullary) surfaces of the bone, leading to U-shaped uranium profiles, and an increasing underestimation of closed-system U-series dates toward the center of the bone. Over time, these uranium concentration profiles gradually flatten until the adsorbed uranium in the bone is at equilibrium with uranium in the groundwater. The parameter t' can be estimated from the measured uranium concentration profiles and U-series isotope profiles generated for different values of t and compared to observations to yield a date.

Furthermore, since adsorption is a reversible process, the D-A model can also predict the leaching of uranium from the bone (e.g., in response to a decrease in uranium concentration in the groundwater) and the overestimation of U-series dates calculated using the EU assumption that many

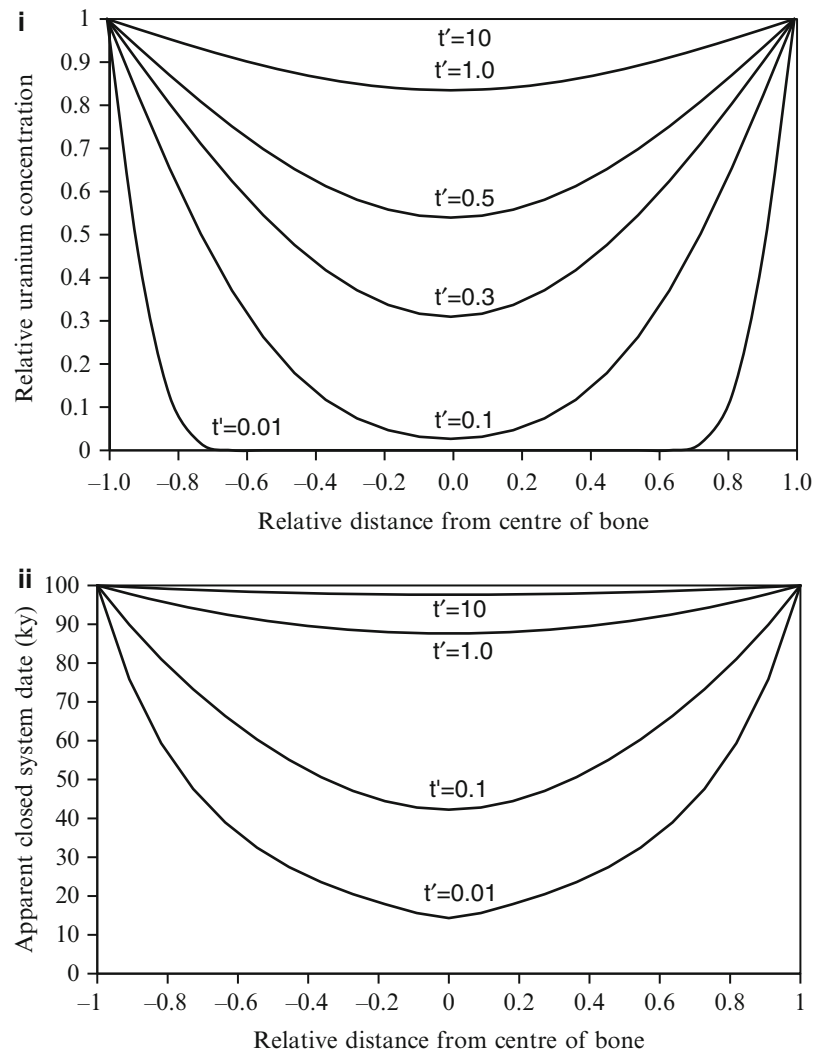


Fig. 1 Simulated U concentration profiles (i) and “date profiles” (ii) across a transverse section of bone predicted by the D-A model under constant geochemical conditions for a 100-ka-old bone. Different curves show the effects for different values of the model parameter t' , which is a function of time and parameters intrinsic to a particular bone. For a given bone, diffusion of U from the edges of the bone leads to a U-shaped U profile that gradually flattens over time until an equilibrium concentration is reached between U in the bone and U in the groundwater. The pattern of apparent closed-system dates shows increased underestimation toward the center of the bone, except where bones equilibrate rapidly (i.e., $t' \gg 1$)

researchers had observed. After initial uptake, a decrease in uranium concentration in the groundwater will lead to desorption of uranium and diffusion in the opposite direction (i.e., out of the bone) and lead to $\cap$ - or M-shaped uranium concentration profiles. As a consequence, $^{230}\text{Th}/^{238}\text{U}$ activity ratios become elevated toward the surface of the bone due to the preferential loss of U relative to Th resulting in overestimates of closed-system U-series dates and elevated initial $^{234}\text{U}/^{238}\text{U}$ activity ratios. Similarly, an increase in the U concentration of the groundwater will lead to increased uptake and characteristic steep gradients of U profiles (Fig. 2).

Pike et al. (2002) compared U concentration and U-series isotope profiles in archaeological bone to those predicted by the model. They found that where both uranium concentration and U-series isotope profiles were U-shaped and agreed with the profiles predicted by the D-A model, open-system dates (calculating using the D-A model) agreed well with control dates. However, these

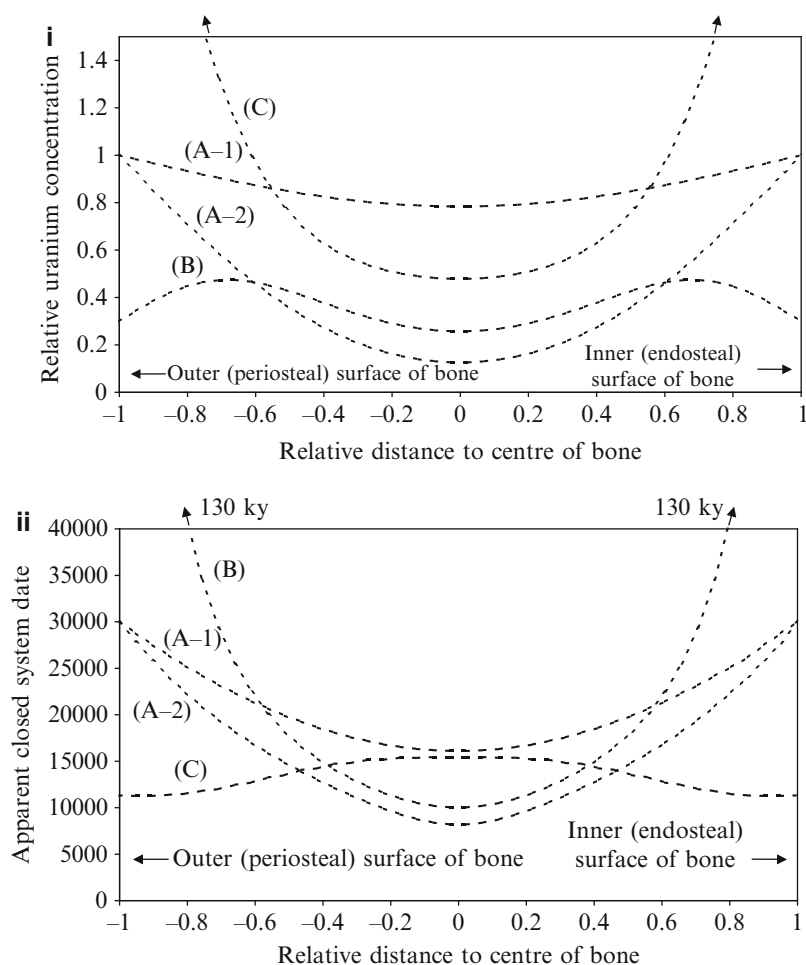


Fig. 2 Simulated U concentration profiles (i) and “date profiles” (ii) across a transverse section of bone predicted by the D-A model for different U uptake regimes for a 30-ka-old bone. Shown in (i) are U concentration profiles predicted for diffusive uptake under constant conditions with the bone nearing equilibrium with the groundwater, i.e., $t' \rightarrow 1$ (A-1); diffusive uptake under constant conditions with the bone far from equilibrium, i.e., $t' \ll 1$ (A-2); leaching of uranium after initial uptake (B); and a recent increase in the uptake of uranium, “recent uptake” (C). Simulated date profiles across the same bone are shown in (ii). Diffusive U uptake under constant conditions (A-1) shows apparent closed-system dates decreasing toward the center of the bone section, although dates are not as underestimated as for bones further from equilibrium with the groundwater (A-2). The leaching of U after initial uptake increases the $^{230}\text{Th}/\text{U}$ resulting in apparent closed-system dates that overestimate the true age, especially toward the outer and inner surfaces of the bone (B). Recent increased U uptake (C) gives underestimated apparent closed-system dates and can lead to a characteristic $\cap$ distribution of dates

bones were in the minority of those examined; many did not appear to have experienced constant geochemical environments. Bones that exhibited leached profiles as well as those that had taken up uranium at an increasing rate (deemed “recent uptake”) were present, as well as those with irregular profiles that may have experienced complex changes in burial geochemistry or diagenetic processes over long timescales. However, Pike’s et al. approach was to reject U-series results from these profiles and only accept results with profiles that conformed to straightforward predictions of the D-A model.

Sampling and Development of Laser Ablation Methods

U concentration and isotope profiles were made on a transverse section, usually a few mm thick, and cut from the bone using a diamond saw. Ideally, this would be a mid-shaft section of long bone for uptake to approximate to the one-dimensional diffusion in an infinite planar slab which is the basis of the D-A model. Other geometries (e.g., of teeth) have been considered (Pike and Hedges 2001), and Crank (1975) gives equations which could be incorporated to adapt the D-A model to radial diffusion and other phenomena. Initially, Pike et al. (2002) used inductively coupled plasma mass spectrometric (ICP-MS) U concentration measurements on 6–10 subsamples drilled from each cross section to create uranium concentration profiles and screen bones for U-series measurement. A second set of subsamples were drilled from selected bones for thermal ionization mass spectrometer (TIMS) measurement of U-series isotopes. This proved analytically costly, and slow, and was subsequently replaced by a method that used laser-ablation multi-collector ICP-MS (Eggins et al. 2003, 2005). For bones with a few ppm of uranium or more, U concentration and U-series isotope profiles could be measured simultaneously using laser ablation, at far higher spatial resolution than by drilling samples (in some cases, several hundred $^{238}\text{U}/^{230}\text{Th}$ per bone section), and typically in less than an hour per bone. Precision on an individual measurement was far poorer than for TIMS, but this is outweighed by the increased precision and accuracy afforded by fitting predicted profiles to data-dense measured profiles. The precision on modeled dates largely depends on the goodness of fit of the measured profiles to the model's predictions and is typically 2–10 % (e.g., see Pike et al. 2005). Millard and Hedges' model was later refined to allow for the evolution of $^{234}\text{U}/^{238}\text{U}$ in the bone within a groundwater with constant $^{234}\text{U}/^{238}\text{U}$ (Sambridge et al. 2012), though as yet it remains unclear to what extent there is exchange between adsorbed uranium and the groundwater, and therefore the evolution of $^{234}\text{U}/^{238}\text{U}$ during uranium uptake remains a significant uncertainty which presumably affects the accuracy of D-A dates where $^{234}\text{U}/^{238}\text{U} \gg 1.0$.

Applications

Because of their size and availability, the majority of applications have been on faunal bones, for example, to constrain the ages of biostratigraphic faunal assemblage zones in the United Kingdom (e.g., Pike et al. 2005) or as a proxy for the age of hominin bones or activity from the same archaeological layer (e.g., Storm et al. 2013), but the ability to date very small samples using laser ablation has opened up the possibility of dating valuable human fossils. These have included direct U-series dates on the Omo-Kibish 1 modern human skull from Ethiopia, confirming the Ar–Ar dating of sediments that suggest an age of close to 195 ky (Aubert et al. 2012), supporting genetic models of the appearance of modern humans in Africa c. 120–220 ka ago (e.g., Ingman et al. 2000). The method has also been used to produce dates of relevance to understanding the migrations of modern humans out of Africa, in particular in regions where the first appearance of modern humans predate the c. 40–50 ka limit of radiocarbon dating, such as a human metatarsal dated to 67 ± 1 ka in Callao Cave, Luzon, Philippines (Mijares et al. 2010), or where collagen preservation is poor, for example, for the Niah Cave deep skull from Borneo dated to 35.2 ± 0.3 ka (Barker et al. 2007; Reynolds et al. 2013). In Europe, several studies have used the method to constrain the timing of the disappearance of the Neanderthals (Walker et al. 2008; Daura et al. 2010; Zilhao et al. 2011), although some of the U-series results were used only to corroborate other dating methods.

Future Directions

One of the key obstacles to more widespread adoption of U-series methods of dating bone is the number of bones that are rejected as unsuitable for dating on the basis of their measured profiles. A large proportion of these are at equilibrium and show uniform U concentration and U-series isotope profiles. A value for t' cannot be estimated from a uniform profile, and thus the rate of equilibration cannot be determined. This is important since diagenetic changes in the bone may increase the rate at which equilibrium is established, raising the possibility that a bone may have re-equilibrated with geochemical changes that would have resulted in the loss or further uptake of uranium (phenomena normally spotted by characteristic profiles). Thus dates from equilibrium profiles are only of use to corroborate other dating methods (e.g., Walker et al. 2008). However, the recent development of ICP methodologies to measure ^{231}Pa at high precision will enable combined U–Th–Pa concordance dating of these samples (e.g., see Cheng et al. 1998) and even perhaps the measurement of $^{235}\text{U}/^{231}\text{Pa}$ profiles to further refine the D-A method.

Summary

Bone is an open system and gains (or loses) uranium from the burial environment, and therefore a model of uranium migration is required to calculate a U-series date from the measured $^{230}\text{Th}/\text{U}$. Early models, based on simple mathematical assumptions, did not yield consistent results, but some success has been had using an explicit geochemical model based on the processes of diffusion and adsorption (the D-A model). The D-A model predicts the spatial distribution of U and U-series isotopes across a bone section, and where these “profiles” indicate the bone has experienced relatively constant geochemical conditions, an open-system date can be calculated.

Cross-References

- ▶ [Apatite](#)
- ▶ [Ar–Ar and K–Ar Dating](#)
- ▶ [Archaeomagnetic Dating](#)
- ▶ [Carbonates, Speleothem Archaeological, \(U-Series\)](#)
- ▶ [Cave Painting \(\$^{14}\text{C}\$ \)](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Luminescence, Archaeological Sediments](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Sediments, Archaeological](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [U-Series Dating](#)

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Carbonates, Lacustrine (U-Series)

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Synonyms

[Aragonitic lake sediments](#); [Calcitic lake sediments](#); [Lake carbonates](#)

Definition

Method of dating late Quaternary geological events (typically up to ~600 ka) by U and Th isotopes in primary calcium carbonates (e.g., aragonitic corals, calcitic speleothems, aragonitic or calcitic lake sediments). The method is based on the radioactive decay of ^{238}U to its daughters ^{234}U and ^{230}Th . The radiometric “clock” measures the time that is required for a particular carbonate system to reach the condition of secular equilibrium after chemical fractionation between soluble U and insoluble Th in waters (e.g., seawater). The isotopes of U and Th can be measured by α -counting or mass spectrometric methods.

Introduction

The U-series dating method is the principal means to establish precise chronologies of late Quaternary geological events by analyses of primary carbonates, those that precipitate chemically from marine and continental water bodies: corals, speleothems, lacustrine sediments, and travertines. Examples are chronologies of sea level changes, coastal tectonic movements, and coastal hydrology (e.g., Edwards et al. 1986; Stein et al. 1993; Lazar and Stein 2011), as well as patterns of continental climate changes by dating primary lacustrine carbonates or cave speleothems (cf. Kaufman 1971; Kaufman et al. 1998; Winograd et al. 1988, 1992; Schramm et al. 2000; Haase-Schramm et al. 2004; McGee et al. 2012; Torfstein et al. 2013a, b). The possibility of obtaining precise U–Th ages on corals stems from the nearly complete chemical separation between U (soluble) and Th (insoluble) in seawater, which results in “clean” precipitation of U within the coral aragonitic skeleton (no initial ^{230}Th and negligible amount of detritus). Lake carbonates, however, typically contain significant amounts of non-authigenic U and Th, and possibly authigenic (hydrogenous) Th, which must be considered in age evaluations (cf. Ku and Liang 1984; Luo and Ku 1991; Kaufman 1993; Lin et al. 1996).

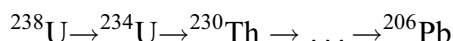
U–Th Dating of “Pure” and “Dirty” Carbonates

The ^{234}U – ^{230}Th dating method is based on the deviation of the intermediate daughter isotopes in the ^{238}U decay series from the state of secular equilibrium. The initial state of the disequilibrium

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condition is produced when U and Th fractionate in a hydrologic environment such as seawater or lake water. This fractionation reflects the distinctly different chemical affinity of U and Th. While U forms soluble complexes in water with various salinities and pH values, Th typically is removed by absorption onto surfaces of sedimentary particles. Thus, the $[^{230}\text{Th}/^{238}\text{U}]$ activity ratio approaches zero in calcium carbonate (CaCO_3) precipitated from the water. Furthermore, the carbonate incorporates U according to the specific partition coefficient that depends on the type of the CaCO_3 mineral phase (e.g., aragonite or calcite) and environmental factors such as water temperature and pH (cf. Lazar et al. 2004).

The condition of secular equilibrium in the decay series



is achieved because the half-life of the parent isotope ^{238}U is much longer than the intermediate daughter isotopes in the series. For the pair ^{234}U – ^{230}Th , the condition of secular equilibrium is typically achieved after ~ 500 ka. The ^{234}U – ^{230}Th “clock” measures the time elapsed from the incorporation of U within the CaCO_3 and the present day (provided that it is less than the time required to achieve secular equilibrium). The incorporation of U in the carbonate mineral phases follows the chemical separation between U and Th in seawater or lake water that leaves the U in solution (as uranyl ion complexes) and removes Th attached to settling particles. Assuming that the precipitated carbonate remained closed with regard to U and Th mobility and that the initial $^{230}\text{Th}/^{238}\text{U}$ is negligible (this may not be the case in system of “dirty carbonates” an issue elaborated below), the equations governing the decay of ^{238}U and ^{230}Th ages that allow the calculation of single ages are (modified after Kaufman and Broecker 1965):

$$\begin{aligned} \left[^{230}\text{Th}/^{238}\text{U} \right]_{\text{act}} &= 1 - \exp(-\lambda_{230}T) + \delta^{234}\text{U}(0)10^{-3} \times [\lambda_{230}/(\lambda_{230} - \lambda_{234})] \\ &\times [1 - \exp((\lambda_{234} - \lambda_{230})T)] \end{aligned} \quad (1)$$

$$\delta^{234}\text{U}(T) = \delta^{234}\text{U}(0) \exp(\lambda_{234}T) \quad (2)$$

where T represents the age, in years, since mineral formation, $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ represents the ratio of ^{230}Th and ^{238}U activities, and λ_{230} and λ_{234} represent radioactive decay constants in years^{-1} for ^{230}Th and ^{234}U , respectively. $\delta^{234}\text{U}(0)$ is defined as the measured activity value $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ recalculated relative to the secular equilibrium value of 1.00 and given in per mil units (‰; i.e.,) $\delta^{234}\text{U} = ([^{234}\text{U}/^{238}\text{U}]_{\text{act, sample}}/1.00) - 1 \times 1,000$. Similarly, $\delta^{234}\text{U}(T)$ is the initial value of $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ calculated at the time of isolation of the specific mineral system (e.g., precipitation of lacustrine aragonite or formation of aragonitic coral, or calcitic speleothem, or travertine). In general, we expect that, for samples representing a simple closed-system evolution, the initial $\delta^{234}\text{U}(T)$ value should reflect the value present in the ambient hydrologic system. Thus corals deposited in seawater will have $\delta^{234}\text{U}(T)$ of ~ 150 (Edwards et al. 1986; Chen et al. 1991; Stein et al. 1993), whereas primary aragonite deposited from the hypersaline lakes in the Dead Sea basin will have $\delta^{234}\text{U}(T)$ of ~ 500 (Haase-Schramm et al. 2004; Torfstein et al. 2013b). Decay constants used in the calculation of the ages are $\lambda_{230} = 9.158 \times 10^{-6}$; $\lambda_{232} = 4.9475 \times 10^{-11}$, $\lambda_{234} = 2.8263 \times 10^{-6}$, and $\lambda_{238} = 1.55125 \times 10^{-10}$ per year (Le Roux and Glendenin 1963; Jaffey et al. 1971; Cheng et al. 2000).

The basic assumptions behind Eq. (1) are *No initial* ^{230}Th is present in the sample and *all of the U* is derived from the ambient water in the depositional habitat. These assumptions hold well for corals,

which typically contain negligible amounts of detrital Th (typically in the range of 0.3–1 pmol/g e.g., Chen et al. 1991; Stein et al. 1993), but rarely holds for other carbonates. Possible interferences in obtaining a true age from measured isotope ratios are U and Th contributed from admixed detritus present in the sample and the possible presence of initial Th in the authigenic (or primary) component.

Correction for the “Detrital” U and Th by the “Isochron” Method

Correction of the U and Th concentrations in “dirty carbonates” is often done by plotting the U and Th activity ratios of a set of coeval samples containing various amounts of detritus on the Rosholt- or Osmond-type “isochron” diagrams. These diagrams are used to identify the $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activities of the “pure primary carbonate.” The $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios of the “detritus-free carbonate” is retrieved from the slopes of “Rosholt”-type diagrams (plots of $^{230}\text{Th}/^{232}\text{Th}$ vs. $^{238}\text{U}/^{232}\text{Th}$ and $^{234}\text{U}/^{232}\text{Th}$ vs. $^{238}\text{U}/^{232}\text{Th}$ activity ratios, respectively) or the y-intercepts of “Osmond”-type diagrams (plots of $^{232}\text{Th}/^{238}\text{U}$ vs. $^{230}\text{Th}/^{238}\text{U}$ and $^{232}\text{Th}/^{238}\text{U}$ vs. $^{234}\text{U}/^{238}\text{U}$ activity ratios, respectively). Alternatively, a “single sample” correction method subtracts the detrital U and Th contributions using either an assumed or measured isotopic composition from individual sample data. The “isochron” approaches have advantages over the single sample correction method when there is a large variation in the mixing proportions of coeval detritus and carbonate samples (cf. Bischoff and Fitzpatrick 1991; Haase-Schramm et al. 2004; Kaufman 1993; Ludwig and Titterton 1994; Torfstein et al. 2013a). Such a set of samples may display a large range of values along a line in “isochron” diagrams and the composition of the detrital end-member may not have to be explicitly assumed.

Correction for Initial Hydrogenous Th

Correction for initial hydrogenous Th in the primary carbonate phase cannot be done by the isochron method. This component might be determined empirically by using a sample of known age determined by independent means (e.g., by ^{14}C ages of organic material). Any apparent difference in the U–Th age could be attributed to the presence of initial ^{230}Th (after correcting for the detritus component). In this case, the extra initial ^{230}Th is corrected by subtracting this component from the detritus-corrected values. Alternatively, the fraction of the hydrogenous Th can be retrieved from analyses of trace element chemistry of specific samples (e.g., Th/Zr ratios, as detailed in Haase-Schramm et al. 2004).

The following sections describe two case studies where U–Th chronologies were established for lacustrine sequences: the last glacial Lake Lisan in the Levant-Dead Sea basin and Lake Bonneville in the western US Great Basin. Other examples of lacustrine deposits that were dated by the U–Th are described by Israelson et al. (1997), Ku et al. (1998), and Lin et al. (1996), among others.

U-Series Dating of Lake Lisan (Last Glacial Dead Sea)

Lake Lisan occupied the tectonic depressions along the Dead Sea Transform fault in the Levant region of the eastern Mediterranean during the last glacial period. The lake comprises Ca-chloride brine that requires the supply of bicarbonate ions to precipitate primary carbonate. This is furnished

by the annual freshwater input. Turbulent mixing across the epilimnion (upper water layer) and hypolimnion resulted in precipitation of primary aragonite (Stein et al. 1997). The excellent preservation and high U concentrations (~3 ppm) of the aragonite make it useful for ^{234}U – ^{230}Th dating. The pioneering attempts in applying this method to Lake Lisan sediments were made by Kaufman and colleagues using α -counting techniques (Kaufman 1971; Kaufman et al. 1992). They showed that, unlike coral samples, the Lisan aragonites are associated with a detrital U and Th component that should be corrected out prior to calculation of ^{234}U – ^{230}Th and applied the “isochron” methods to perform these corrections. With the development of the TIMS method for analyzing U and Th isotopes in small carbonate samples, Schramm et al. (2000) and Haase-Schramm et al. (2004) measured U and Th abundances in a stratigraphic section of the Lisan Formation (PZ1 section at Perazim Valley), corrected for detritus U and Th and hydrogenic Th and established an age-height chronological model for the time interval of 70–14 ka BP. Recently, Torfstein et al. (2013a) used the plasma machine (ICP-MS-MC) to analyze the U and Th isotope in several stratigraphic sections of the Lisan Formation in the Dead Sea-Jordan Valley and established an integrated multi-site U–Th chronology for the Lisan Formation. The U–Th Lisan chronology has been used for paleoclimate and paleoseismic studies and for calibrating the radiocarbon time scale in the last glacial time interval (Haase-Schramm et al. 2004; Bartov et al. 2003; Kolodny et al. 2005; Torfstein et al. 2013a, b).

U-Series Dating of Lake Bonneville

Lake Bonneville, which occupied the Bonneville Basin of the northeastern Great Basin (USA), experienced a lake level history very similar to the Levant-Lake Lisan, approaching its highest stands during the last glacial ~26 ka BP and commenced its deglacial retreat after ~16 ka BP (Oviatt et al. 1990, 1992). Nevertheless, the reconstruction of lake paleohydrology and paleolimnology suffered from lack of accurate chronologies (e.g., uncertainties in the radiocarbon reservoir ages). Recently, new chronological constraints on the glacial and postglacial history of the lake were achieved by U–Th dating of lacustrine cave carbonates (McGee et al. 2012). The cave carbonates provide a promising new archive of past hydrologic changes in the Bonneville Basin. The carbonates precipitated within caves (e.g., Cathedral and Craners caves), crevices, and other protected spaces flooded by Lake Bonneville during its high stand in the last glacial period. The caves are located at similar elevations approximately 100 m above the modern Great Salt Lake and almost 200 m below Lake Bonneville’s highstand shoreline. Precise U–Th ages determined on the cave carbonates indicate a minimal (~200 y) radiocarbon reservoir age in the lake and allows ^{14}C dating to be used for age control in portions of the deposits less suitable for U–Th dating. The combined U–Th and radiocarbon data document the timing of the lake’s transgression between 26 and 18 ka and a large influx of fresh water during Heinrich Stadial 2. This was reflected by a hiatus in calcite deposition. Calcite deposition resumed at ~16.4 ka, suggesting that basin overflow had ceased by this time. The lake’s deglacial regression began ~16 ka. Cessation of this second phase of deposition at 14.7 ± 0.2 ka, coincident with the Bølling-Allerød warming, may reflect the lake’s drop below Cathedral Cave’s elevation. Overall, the Great Basin (USA) Bonneville lacustrine system and the Dead Sea-Lake Lisan (Levant) show very similar responds to the global climate, which demonstrates the great potential in performing precise U–Th dating on the lacustrine carbonate deposits.

Concluding Comments

U–Th dating of lacustrine (authigenic or primary) calcium carbonates is a prime method of achieving accurate and high-resolution chronologies for the geochemical-limnological evolution of late Pleistocene lakes. However, the lake carbonates are typically “contaminated” by detrital U and Th and initial hydrogenous Th. Application of the “isochron methods” (e.g., Rosholt- or Osmond-type diagrams), combined with stratigraphical considerations, independent dating methods, such as radiocarbon over the past 50 ka, and oxygen isotope chronologies, helps to derive reliable and high-resolution chronologies for the lacustrine sequences.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Carbonates, Marine \(\$^{14}\text{C}\$ \)](#)
- ▶ [Carbonates, Marine Carbonates, \(U-Series\)](#)
- ▶ [Carbonates, Speleothem Climatic, \(U-Series\)](#)
- ▶ [Cements, Pedogenic \(U-Series\)](#)
- ▶ [Geochronology](#)
- ▶ [Lacustrine Environments \(\$^{14}\text{C}\$ \)](#)
- ▶ [Lacustrine Varves](#)
- ▶ [Luminescence, Deep Sea Marine and Lacustrine](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [U-Series Dating](#)

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Carbonates, Marine Carbonates, (U-Series)

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Synonyms

Coral dating; ^{238}U - ^{234}U - ^{230}Th dating; U-series chronology; U-Th dating

Definition

U-series nuclides. Nuclides of the ^{238}U , ^{235}U , and ^{232}Th radioactive decay chains, which begin with the above radioactive nuclides and end with a stable isotope of lead.

Fractionation. The fractional gain or loss of one element relative to another (*elemental fractionation*) or one isotope relative to another of the same element (*isotopic fractionation*) during geological events.

Decay constant. The proportionality constant of a radionuclide defining the number of atoms decaying over a given period of time compared with the number of atoms present initially.

Mass spectrometry. An analytical technique that produces spectra of the masses of molecules or atoms used to determine the isotopic composition of a sample. Particles are ionized in the instrument source followed by physical separation based on their mass-to-charge ratio.

Introduction

For the last 800 millennia, climate has oscillated between cool ice ages and warmer interglacial conditions with a periodicity of about 100 thousand years. For example, during the “Last Deglaciation” between about 21 and 6 thousand years ago (ka), more than 50 million cubic kilometers of ice melted from the major continental ice sheets, raising the sea level by ~130 m (Lambeck et al. 2002). The waxing and waning of the ice sheets, fall and rise in sea level, and the cooling and warming of Earth’s climate are faithfully preserved as compositional changes in marine sediment records (Lisiecki and Raymo 2005) (Fig. 1a). These archives provide continuous, high-resolution records of past climate change but lack critical information on absolute timing because they cannot be directly dated, relying instead on model chronologies (Milankovitch 1941) that require further validation. As a result, the exact mechanisms driving the Earth’s natural climate cycles remain uncertain. Obtaining reliable, absolutely dated records of past climate change is critical for understanding how Earth’s natural climate cycles work. These data can provide a firmer basis for assessing the role of anthropogenic effects, such as greenhouse gas emissions, in modifying climate, thus improving twenty-first-century climate projections.

In-built clocks based on the decay of radioactive elements that are present in minute quantities in rocks and sediments allow an absolute chronology to be assigned to geological records. One of the key dating methods used in paleoclimate research takes advantage of the natural radioactive decay of

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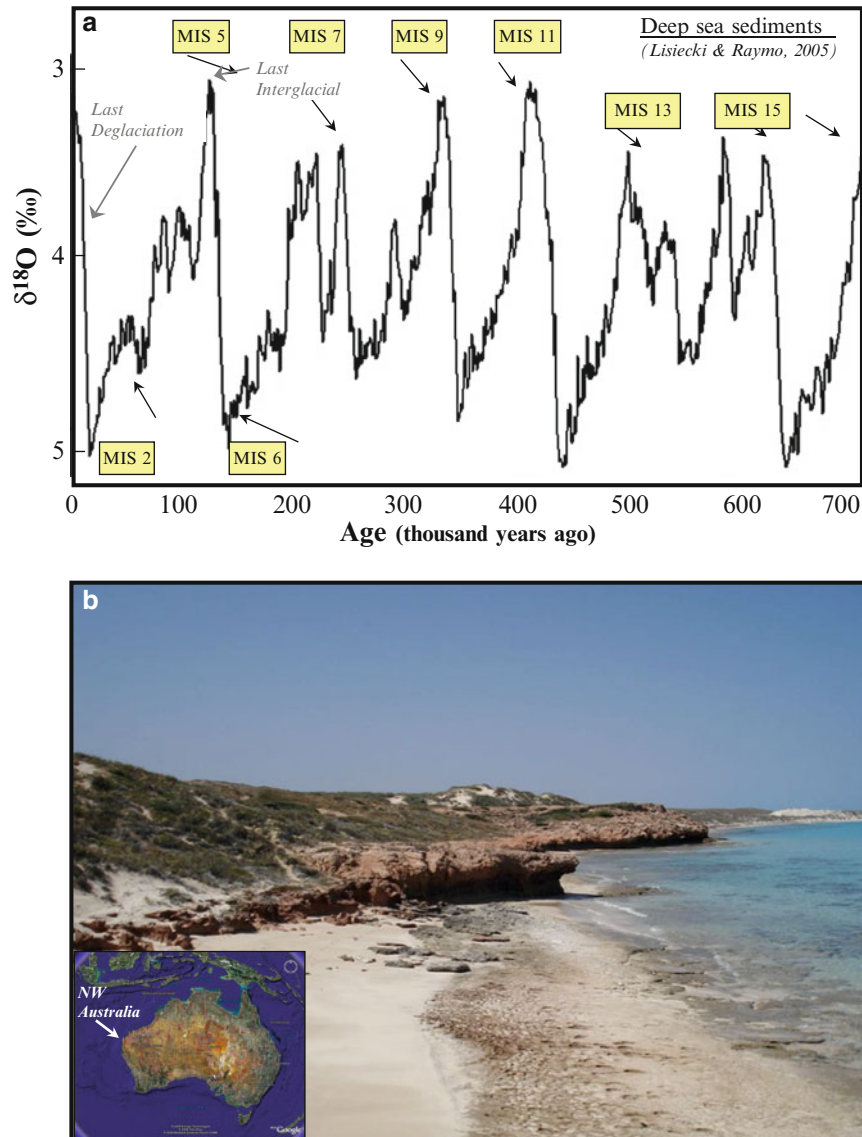


Fig. 1 (a) The LR04 deep-sea sediment oxygen stable isotope ($\delta^{18}\text{O}$) record, which comprises a stack of 57 globally distributed deep-sea records and provides a combined signal of deep-ocean temperature and global sea level for the past 5.3 million years (Lisiecki and Raymo 2005). The past 700 thousand years of this record is shown and has been assigned a timescale by direct correlation with model chronologies. Glacial-interglacial climate episodes are defined by “marine isotope stage” (or MIS) terminology, whereby even- and odd-numbered MIS intervals refer to glacial and interglacial periods, respectively. Distinct oscillations between warm interglacial periods (high $\delta^{18}\text{O}$ values) and cool glaciations (low $\delta^{18}\text{O}$ values) are apparent. Centennial- and millennial-scale climate variability is also evident. (b) Photograph of an elevated “Last Interglacial” fossil coral reef, within a few meters of the present shoreline, along the coast of Western Australia which formed around 125,000 years ago. Fossil corals within the reef framework can be directly dated using the U-series dating method

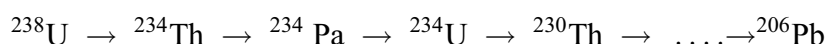
uranium (U) to thorium (Th) in U-bearing minerals, such as calcium carbonate. This technique, commonly referred to as the U-series dating method (Broecker 1963), has been widely applied to the following shallow-water marine carbonate archives in the reconstruction of past climate. Results have provided constraints on the precise timing, duration, and magnitude of key climate episodes:

1. *Shallow-water reef-building corals*. These archives grow close to the sea surface, providing valuable information on both sea-level and ocean-water temperature fluctuations, particularly during interglacial sea-level high stands when reefs grow prolifically (Broecker 1963; Edwards et al. 1987). The stratigraphic and morphological structures of the reef, combined with the height-age relationships of fossil corals within the reef framework, can be used to reconstruct the reef's growth history and, in turn, derive local sea-level curves for the study locality (Fig. 1b).
2. *Calcium carbonate slope sediments*. Calcium carbonate sediments, such as those swept from the banks of the Bahamas, yield continuous sea-level and climate records, especially during interglacial periods when the banks are flooded and sediment accumulation rates are high. Records are derived by combining the U-series ages of the carbonate fraction of the sediment with the oxygen stable isotope signatures of foraminifera (marine plankton) that have been deposited simultaneously (Slowey et al. 1996).
3. *Submerged coastal speleothems (stalagmites and stalactites)*. These archives are currently found below sea level in coastal caves. Calcium carbonate growth occurs during sea-level low stands when the caves are emergent, whereas growth ceases during flooding by rising sea levels. Important information on the timing, duration, and elevation of sea-level low stands and marine transgressions can be obtained by dating the carbonate preserved on either side of a growth hiatus (Richards and Dorale 2003).

The U-series dating method has also been applied to deepwater marine carbonates, including deep-sea solitary corals and chimney deposits (Teichert et al. 2003; Robinson et al. 2005).

Basic Principles of the U-Series Chronometer

The U-series dating method utilizes the natural radioactive decay of ^{238}U to its longest-lived intermediate daughters, ^{234}U and ^{230}Th , and subsequent decay, via a series of short-lived nuclides, to stable ^{206}Pb as follows:



Half-life	4.5 billion years	24 days	1 min	245 thousand years	76 thousand years	Stable
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The respective 245,000 and 76,000 year half-lives of ^{234}U and ^{230}Th make the U-series system particularly useful for dating climate events spanning the last 600,000 years.

U-Series Nuclides in the Modern Global Ocean

For the U-series system, a state of *radioactive equilibrium* occurs when the activities, or rates of decay or in-growth, of ^{234}U and ^{230}Th , and all other intermediate daughters in the ^{238}U decay chain, are equal and identical to the activity of ^{238}U . This condition is achieved after five or six half-lives of the daughter isotope, provided that the system is left undisturbed without being subjected to parent-daughter fractionation events. In this state, the activity ratios between ^{238}U and its ^{234}U and ^{230}Th daughters, referred to as $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}}$ and $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]_{\text{act}}$, respectively, are invariant and equal to unity, irrespective of the time elapsed. After this point, the system cannot be used as a dating tool. Importantly, the U-series dating of marine carbonates becomes possible because chemical and nuclear processes continuously disrupt the state of U-series radioactive equilibrium in modern

hydrological systems. This gives rise to the following two conditions of *radioactive disequilibrium* in the marine environment, allowing the $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}}$ and $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]_{\text{act}}$ ratios of marine minerals to evolve to a new equilibrium state as a predictable function of time:

1. There is an extreme chemical fractionation between U and Th in the oxygenated modern ocean. In particular, U is present in its highest U(VI) oxidation state and forms uranyl complexes that are highly soluble in seawater. In contrast, Th exists as relatively insoluble species in the Th(IV) oxidation state, yielding negligible levels of dissolved Th in the global ocean (Ivanovitch and Harmon 1992).
2. The state of radioactive equilibrium between ^{238}U and ^{234}U is also disrupted due to internal damage to mineral grains during the energetic decay of ^{238}U . As a result, the ^{234}U daughter nuclide is often only loosely bound to the mineral structure, making it more susceptible to preferential leaching during weathering than lattice-bound ^{238}U (Ivanovitch and Harmon 1992). Consequently, seawater contains an ~15 % excess of ^{234}U over ^{238}U (i.e., seawater $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}} = 1.15$) compared to the radioactive equilibrium value of 1.00 due to steady-state input by river water loaded with dissolved U from continental weathering processes (Edwards et al. 2003).

U-Series Nuclides in Modern Marine Carbonates

During the formation of marine carbonates, the ^{238}U , ^{234}U , and ^{230}Th isotopes are removed from seawater, together with other dissolved metals, and incorporated into the mineral structure. Thus, newly formed corals, speleothems, and aragonitic slope sediments contain U with a “disequilibrium” initial $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}}$ ratio of 1.15, but no significant ^{230}Th (Edwards et al. 2003). Following calcium carbonate formation, the U-series nuclides become isolated from the steady-state ocean (where decaying nuclides are continuously resupplied from riverine and other sources), allowing the ^{234}U and ^{230}Th intermediate daughters to evolve to a new equilibrium state with their ^{238}U parent as a predictable function of the time elapsed since the mineral developed. Thus, for every marine carbonate sample, both the radioactive decay of ^{234}U and the simultaneous in-growth of ^{230}Th toward radioactive equilibrium with ^{238}U can be expressed as a function of its U-series or ^{230}Th age, denoted by T, provided that (1) $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]_{\text{act}}$ and $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]_{\text{act}}$ can be reliably measured and (2) the decay constants for ^{234}U and ^{230}Th (λ_{234} and λ_{230} , respectively) are accurately known. This relationship is shown in Fig. 2 and Eq. (1), and T can be calculated iteratively (Edwards et al. 1987):

$$1 - \left[\frac{^{230}\text{Th}}{^{238}\text{U}} \right]_{\text{act}} = e^{-\lambda_{230}T} - \left(\left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_{\text{act}} - 1 \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left(1 - e^{(\lambda_{234} - \lambda_{230})T} \right) \quad (1)$$

The ^{230}Th age will accurately reflect the “true” age of the sample, provided that (1) no initial ^{230}Th existed in the sample at the time of its formation and (2) no further gain nor loss of the U-series isotopes takes place other than by “closed-system” radioactive in-growth and decay (Edwards et al. 1987). The latter assumption is sometimes violated, especially in older samples affected by secondary alteration, which tends to disturb the U-series isotopes, offsetting the ^{230}Th age from the true sample age.

Analysis of the U-Series Isotopes

Chemical procedures using ion-exchange resins to selectively adsorb and desorb the elements of interest are typically adopted to isolate “pure” U and Th from the calcium carbonate matrix of the

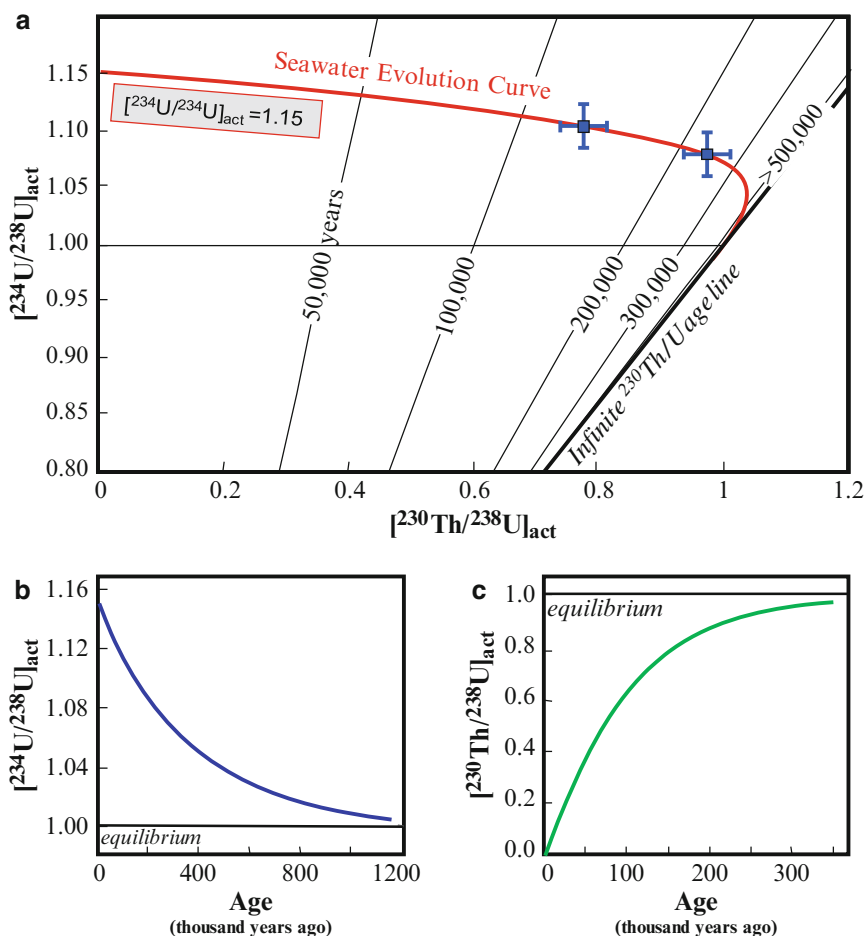


Fig. 2 (a) Plot showing the isotopic evolution of $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ values as a function of time (T). Isochrons (straight, steeply sloping lines) are shown at 50, 100, 200, 300, and 500 ka. The red curve starting at $[^{234}\text{U}/^{238}\text{U}]_{\text{act}} = 1.15$ and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}} = 0$ gives the “seawater evolution path” for a sample formed in the marine environment with U equivalent to the $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ composition of seawater but no Th at the time of its formation. (b) Isotope evolution curve for $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ starting at an initial value of 1.15 evolves by radioactive decay towards the radioactive equilibrium value of 1.0 with time. (c) Isotope evolution curve for $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ starting at an initial value of 0 evolves by radioactive in-growth towards the radioactive equilibrium value of 1.0. Age resolution of the U-series dating method decreases with increasing sample age due to the progressive decrease in separation between isochrons, as demonstrated by the two data points shown in (a) for 125,000- and 200,000-year-old samples measured with identical levels of precision

sample (Goldstein and Stirling 2003). This purification procedure enables the $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ ratios to be reliably determined, free of analytical artifacts such as isobaric or molecular interferences.

Analytical measurements of $[^{234}\text{U}/^{238}\text{U}]_{\text{act}}$ and $[^{230}\text{Th}/^{238}\text{U}]_{\text{act}}$ have an associated uncertainty, which, by convention, is reported at the 2-sigma level. Propagation of these uncertainties through the above U-series age equation results in ^{230}Th -age errors that become proportionally larger with increasing sample age, as radioactive equilibrium is approached and the rate of radioactive decay and in-growth of ^{234}U and ^{230}Th slows down (Fig. 2). This progressive loss in the resolution of the U-series chronometer with increasing age demonstrates the importance of achieving the highest analytical precisions possible.

To this end, the U-series dating method has benefitted enormously from ongoing innovations in technology that have occurred over the past 30 years. In particular, the advent of thermal ionization mass spectrometry (TIMS) in the 1980s and, more recently, multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) in the late 1990s to U-series isotopic analysis dramatically reduced sample-size requirements, shortened analysis times, and improved measurement precision compared with earlier decay-counting techniques using alpha spectrometry (Goldstein and Stirling 2003). Ongoing design improvements in instrumentation over the last 10 years have continued to enhance U-series analytical performance (Stirling and Andersen 2009). As a result, ^{230}Th -age uncertainties of ± 800 years in 120,000-year-old samples and $\pm 3,000$ years in 300,000-year-old samples can now be routinely achieved. Some recent studies have further improved ^{230}Th -age uncertainties to better than $\pm 1,000$ years in 300,000-year-old samples (Stirling and Andersen 2009).

U-Series Dating to Marine Carbonates: Windows into Past Climate

Over the past two decades, the U-series dating of marine carbonates has provided crucial new constraints on the absolute timing and duration of key climate intervals throughout the past 600 thousand years of the Earth's climate history. At the young end of the dating range, U-series measurements have been used to determine the timing and frequency of El Niño events, occurring over the past few centuries (Edwards et al. 2003). In the $< 50,000$ -year range, coupled U-series and $^{14}\text{C}/^{12}\text{C}$ measurements for deep-sea corals have been used to constrain ventilation and circulation patterns of oceanic water masses and how they regulate global climate (Robinson et al. 2005). Furthermore, U-series measurements for drilled fossil coral reefs have been used to calibrate the ^{14}C chronometer for the past 40,000 years (Edwards et al. 2003). These drill-core coral data also provide a continuous record of sea-level rise and climate change for the "Last Deglaciation," extending from the peak of the last glacial maximum to the onset of the present interglacial warm period, from around 21 to 6 thousand years ago (Edwards et al. 2003; Deschamps et al. 2012). These results are discussed in more detail as follows:

The Last Deglaciation: Collectively, records from core drilled at coral reefs show evidence for several distinct "meltwater pulses" rather than continuous melting during the Last Deglaciation due to episodic periods of rapid ice sheet retreat. The largest of these events, referred to as "meltwater pulse" (MWP)-1A, occurring around 14 thousand years ago, produced an extremely rapid sea-level rise of ~ 20 m over 300 years, which is in excess of 40 m/1,000 years and approximately ten times faster than present melting rates. This was succeeded by the abrupt "Younger Dryas" cooling event, involving a transient return to full ice age conditions at ~ 12 ka before renewed sea-level rise. These abrupt centennial- to millennial-scale oscillations in climate and sea level appear synchronous with large-scale reorganization of North Atlantic thermohaline circulation, an oceanic conveyor belt exporting heat from the tropics to the poles. However, there is no consensus on the geographic source of meltwater during deglaciation nor exact underlying mechanisms controlling rapid sea-level and climate change. Recent U-series dating of drill core from fossil corals at different locations worldwide provides high-resolution "fingerprinting" of MWP-1A and implicates a substantial contribution of meltwater from the ice sheets of both northern and southern hemispheres (Deschamps et al. 2012). This suggests that melting of both the Greenland and Antarctic ice sheets will be highly sensitive to sustained global warming in the coming decades and may already be contributing to present day sea-level rise.

Prior to the last 50,000 years, a wealth of information is available only for the Last Interglacial period, occurring around 125 thousand years ago (discussed below). This is primarily because marine carbonates that formed close to modern shorelines during this time are relatively accessible for study today (Stirling and Andersen 2009).

The Last Interglacial period: The Last Interglacial interval, occurring from approximately 128 to 116 thousand years ago (Stirling and Andersen 2009), represents that the last time global sea levels were at or near modern levels and, by inference, the last time global climatic conditions, as well as the size and configuration of the major ice sheets, were similar to those in the present day. The Last Interglacial period has therefore been identified as a suitable analogue of the present climate system in order to speculate on future climate trends. Importantly, the Last Interglacial temperatures are likely to have been similar to, or slightly warmer, than the preindustrial state. Therefore, a reliable assessment of the timing, duration, and amplitude of global sea levels during the Last Interglacial is crucial for assessing the stability of the today's ice sheets in response to climate warming of a few degrees. Dutton and Lambeck (2012) have recently compiled all available U-series data for the Last Interglacial fossil reefs, demonstrating that the Last Interglacial global sea levels peaked between 5.5 and 9 m above the present sea level. These amplitudes require smaller ice sheets in both Greenland and Antarctica relative to today, implying a strong sensitivity of the cryogenic system to only minor climate warming.

Marine carbonates formed earlier than 125,000 years ago are prone to secondary alteration. Going forward, one of the key challenges faced by the U-series community is to acquire reliably dated climatic records for earlier interglacial periods that could represent more suitable analogues of the present climate system than the Last Interglacial period, such as “marine isotope stage” 9, 11, or 15 (Fig. 1) (Stirling and Andersen 2009).

Summary

The U-series dating of marine carbonates is based on the natural radioactive decay of ^{238}U to its longest-lived intermediate daughters, ^{234}U and ^{230}Th . This technique has been used to provide reliable, accurately dated records of past sea-level and climate change for the past 600,000 years of the Earth's history, especially for the past 130,000 years of the last glacial-interglacial cycle. This, in turn, has facilitated a more complete understanding of the mechanisms driving the Earth's natural climate cycles, which have helped to inform projections of twenty-first-century climate change.

Cross-References

- ▶ [Alpha Spectroscopy](#)
- ▶ [Carbonates, Marine \(14C\)](#)
- ▶ [Carbonates, Speleothem Climatic, \(U-Series\)](#)
- ▶ [Corals \(Sclerochronology\)](#)
- ▶ [Geochronology](#)
- ▶ [Luminescence, Deep Sea Marine and Lacustrine](#)
- ▶ [Marine Isotope Stratigraphy](#)
- ▶ [Marine Varves](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Sea-Level Change \(U-Series\)](#)
- ▶ [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- ▶ [U-Series Dating](#)
- ▶ [Uranium Series, Marine Sedimentation Rate](#)

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Carbonates, Speleothem Archaeological (U-Series)

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Definition

Archaeological carbonate speleothems: Deposits of secondary carbonate minerals (usually calcite or aragonite consisting of CaCO_3) that formed in caves containing artefacts or other evidence of past human or hominid occupation

Introduction

U-series dating such as U-Th (or $^{230}\text{Th}/\text{U}$) is a well-established, accurate, and precise method with a wide range of applications in earth sciences, palaeoclimate research, and archaeology (Bourdon et al. 2003). U-series dating can be used to determine the age of materials that formed with a well-constrained radioactive disequilibrium between U and its daughter isotopes, including precipitates of calcium carbonate (CaCO_3) in cave environments, i.e., speleothems like stalagmites, stalactites, or flowstones. U-series dating is essential for palaeoclimate research using speleothems but is less commonly used for archaeological applications. However, cave environments are often associated with archaeology and archaeological finds. Excavations in caves often exhibit stratigraphic relationships with speleothem formation. Where a stratigraphy can be unambiguously established between archaeology and CaCO_3 formation, U-series dating provides a powerful chronological tool and can be applied to constrain minimum and/or maximum ages for associated archaeological finds.

Basic Principles of U-Series Dating of Speleothems

U-Th dating can be applied to materials like secondary CaCO_3 that incorporate disequilibrium between U (^{238}U and ^{234}U) and the daughter isotope ^{230}Th at the time of formation. For example, speleothems such as stalagmites or flowstones precipitate from percolating waters entering a cave. The water also contains trace elements dissolved from host rock above the cave, including U, which are subsequently incorporated in the CaCO_3 . The key for U-Th dating is the difference in solubility between U and Th which leads to elemental fractionation in the percolating water. In contrast to U, Th is largely insoluble and thus not incorporated in secondary carbonates when they form from drip waters in cave environments. Thereafter, ^{230}Th starts to build up until radioactive equilibrium is reached. The return of isotope activities to equilibrium allows quantification of time, i.e., the present $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ activity ratios enable calculation of the time since formation.

The reliability of U-Th ages strongly depends on whether the dated material has remained as a so-called closed system, i.e., U and Th isotopes are neither lost nor gained after precipitation, and whether any initial ^{230}Th was present. Presence of initial (or detrital) Th is tested by determining the

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abundance of common Th (^{232}Th) in the sample. In case of significant amounts of ^{232}Th , a correction for initial ^{230}Th needs to be applied by mathematically subtracting an assumed or measured detrital component or by using “isochron” methods (Ludwig and Titterton 1994).

A single U-Th age does not provide a means of confirming that the dated material represents a closed system. However, there are ways to check reliability of U-Th ages of speleothems with respect to closed-system behaviour. The most rigorous test is to employ the alternative ^{235}U -series chronometer and measure $^{231}\text{Pa}/^{235}\text{U}$ in addition to $^{230}\text{Th}/\text{U}$ on the same material (Cheng et al. 1998). However, U-Pa dating requires much larger sample sizes due to the significantly smaller concentrations of ^{235}U relative to ^{238}U ($^{235}\text{U}/^{238}\text{U} = 0.0073$) and thus cannot be employed in all cases, especially where sample size is limited. Alternatively, where open-system behaviour cannot be excluded, it is recommended to perform repeat U-Th analyses of coeval samples. If dating results on different subsamples are concordant, the system can be regarded as closed. Stalagmites, flowstones, or other carbonates that form with internal stratigraphic constraints provide an additional possibility to check reliability by comparing ages of subsamples precipitated successively along a growth axis, which must become progressively younger from bottom to top.

U-Series Isotope Measurements and Sample Sizes

The applicability of U-series methods depends on availability of sufficient suitable material for dating. In many cases only small samples of less than 100 mg CaCO_3 are available, making the sample size critical. Recent advances in thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) instrumentation and protocols not only led to very high precision measurements of U-series ratios (Andersen et al. 2004; Potter et al. 2005) but also greatly reduced the sample size needed for a precise U-Th age. Currently, sample sizes between 10 and 100 mg are sufficient in most cases (Hoffmann 2008; Hoffmann et al. 2009). Overall, the ability to work on small samples in the range of 10 mg is now the key to many applications in archaeology where only very small sections or thin layers of CaCO_3 are found to have direct stratigraphic relations to archaeological finds.

U-Series Age Constraints for Excavations in Cave Environments

U-series dating has been applied to speleothems from archaeological sites for over 40 years employing alpha spectrometry (e.g., Fornaciari 1968; Schwarcz and Blackwell 1983; Blackwell et al. 1983), TIMS (e.g., Shen et al. 2001; Zhao et al. 2001) or more recently MC-ICPMS techniques (e.g., Mercader et al. 2009; Clark-Balzan et al. 2012; Hoffmann et al. 2013). Generally, sediment fillings in caves containing archaeology can often be found on top of flowstone formations or are covered by a layer of flowstone or in some cases both. Flowstone thus formed before or after artefact-hosting sediments accumulated, and U-series dating of such speleothems provides maximum or/and minimum ages for bracketed sediments. Similarly, stalagmites that form locally on top of sediments at a drip site or that are covered by sediment fill also may provide age constraints for the sediments. The stratigraphy between carbonate deposits and archaeology bearing sediments is essential; only carbonates with unambiguous relationships provide diagnostic ages of the target sediments and should be analysed.

For capping flowstones, the lowest layer is closest in age to the underlying sediment, and for underlying flowstones, the uppermost layer. However, the layers in contact with sediments are also

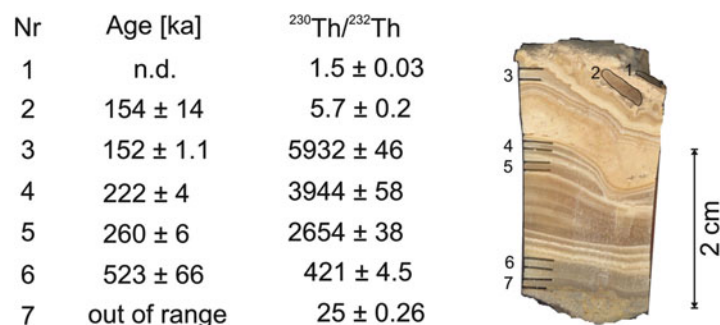


Fig. 1 Example of subsamples and U-series results for a section of flowstone (see text for details)

most prone to incorporation of silicate detritus (dirt) within the carbonate matrix and therefore do not necessarily yield the best dating results. Thus, in most cases, subsamples of detritus-poor carbonate should be taken from a layer within several mm of the flowstone–sediment boundary. It is generally recommended to target subsamples from the most pristine and cleanest parts of the speleothem. It is also essential to perform repeat analyses of a single growth layer and/or a suite of subsamples along the growth axis to verify the presence of closed-system behaviour. In samples that contain high detrital components, “isochron” methods may need to be applied (Ludwig and Titterton 1994).

An example of a 3 cm thick flowstone section is shown in Fig. 1. A cross section of the flowstone was cut and polished for better visibility of growth layers which can clearly be distinguished by colour differences between lighter and darker bands. The top of the flowstone is less dense with a microcrystalline structure and dirt inclusions indicating that this part of the specimen is not suitable for U-Th dating. The bottom of the flowstone is denser but also shows substantial amounts of dirt incorporated in the calcite. Five subsamples were obtained from this section by sawing cuts parallel to growth layers using a diamond wire saw and breaking off small solid pieces using a scalpel (subsamples 3–7). Two additional powder samples (subsamples 1 and 2) were drilled from the top of the section with a handheld micro drill.

The measured $^{230}\text{Th}/^{232}\text{Th}$ activity ratios shown in Fig. 1 indicate the degree of contamination with detrital material. Typical bulk earth detritus has a $^{230}\text{Th}/^{232}\text{Th}$ activity ratio of 0.8 ± 0.4 . The value of 1.5 for the topmost subsample confirms that this part of the section has high dirt content. Consequently, the resulting U-Th isotope data are dominated by the detrital component, and a reliable U-series age cannot be calculated for this subsample. Subsample 2 also shows a high detrital component; however, an age can be calculated for this analysis using a bulk earth Th-correction, although the large correction leads to high dating uncertainty. The results of subsamples 3–6 have $^{230}\text{Th}/^{232}\text{Th}$ activity ratios >400 indicating that negligible detritus is included. Calculated ages require little correction and are in stratigraphic order indicating reliable results. In the case of this flowstone, U-Th dating constrains the underlying sediments to be older than 500 ka and the overlying to be younger than 150 ka.

Buried stalagmites, stalactites, or soda straws have also been suggested to provide age constraints for sediment fills in caves (Schwarcz and Blackwell 1992; St Pierre et al. 2009). Speleothem fragments such as broken soda straws can often be found mixed into cave sediments and must have formed prior to the sediment accumulation. U-series ages of these materials thus can provide a maximum age of the sediment in which they are found.

U-Series Age Constraints for Artefacts and Cave Art

In cave environments, artefacts (bones, tools) or archaeologically relevant sections such as painted cave walls may become exposed to percolating waters and subsequently covered by secondary carbonates. In most cases, only very thin layers of CaCO_3 are found on artefacts, which poses a major restriction for application of U-series dating. Reliable U-series ages can only be obtained where sufficient amounts of CaCO_3 can be removed from the artefacts and where the CaCO_3 has unambiguous stratigraphic relations to the artefacts. Since the calcite formation postdates the archaeology, its age provides a minimum age constraint. For example, Frank et al. (2002) constrained the age of Trojan artificial water-supply tunnels by dating calcite that formed on the tunnel walls. Fu et al. (2008) used calcite coatings to constrain the age of human skeleton fragments from northeastern China.

U-series dating of calcite formations covering cave art was first suggested by Schwarcz and Blackwell (1992) as a future application to provide minimum ages for the underlying art. In most cases, the amount of calcite coating cave art with unambiguous stratigraphic relationship is limited, and availability of sufficient sample size was the major obstruction of U-series dating of cave art. A few studies on cave art dating using TIMS have been published, e.g., Bischoff et al. (2003), Plagnes et al. (2003), or Pike et al. (2005). Dating cave art using U-series methods is now possible for a much wider range of paintings (motifs) again due to the significant reduction of sample material needed for precise U-series measurements (Hellstrom 2012). This enables to work on very small carbonate samples allowing dating of tiny samples scraped from calcite layers covering cave art (Fig. 2). For example, calcite crusts coating cave paintings from over 50 motifs in northern Spain have been dated using this method yielding minimum ages between 500 a and 40,800 a (Pike et al. 2012).



Fig. 2 Sampling of calcite crusts covering cave art: after identification of suitable calcite formation with clear stratigraphic relationship to the cave painting, first the surface of the section is scraped off to remove potential dust contamination and expose the calcite surface for inspection of mineral structure. Then calcite sample is scraped off with a scalpel and collected either directly in a pre-cleaned sample container (*left*) or onto a clean tray. Scraping is stopped as soon as paint becomes visible underlying the sample position (Photos: C. Hoffmann, J. Zilhão)

Summary and Conclusions

In cave environments, archaeologically relevant sections or artefacts can be found with stratigraphic relations to secondary calcite deposits which can be dated by U-series methods. State-of-the-art U-series techniques minimize sample sizes and thus allow selection of the most suitable calcite formations to provide many possibilities for employing this technique in archaeological contexts. The stratigraphic relations between calcite formation and archaeology need to be unambiguous in order to use U-series ages of calcite to constrain the age of archaeological finds and provide minimum or maximum ages.

Cross-References

- [Carbonates, Speleothem Climatic, \(U-Series\)](#)
- [Geochronology](#)
- [Mass Spectrometry](#)
- [Sediments, Archaeological](#)
- [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- [Uranium Series Dating](#)

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Carbonates, Speleothem Climatic (U-Series)

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Synonyms

Carbonates: calcite, aragonite

Speleothem: cave deposit, stalactite, stalagmite, flowstone

Climatic: proxy climate data

U-series: $^{230}\text{Th}/\text{U}$ dating, U-series disequilibrium

Definition

Carbonates. Strictly, a salt of the anion group CO_3^{2-} , but here refers specifically to calcium carbonates, generally associated with limestones (i.e., calcite and aragonite).

Speleothem. A secondary carbonate precipitate formed in a cave void by degassing of CO_2 from supersaturated waters. By far the most common speleothems used for the investigation of past climate are gravity-fed dripstones, such as stalagmites or flowstones formed in the vadose zone, as opposed to phreatic examples formed at or below the water table.

Uranium-series dating. Chronological tool based on the state of disequilibrium in the U-series decay chains. Generally refers to ^{238}U – ^{234}U – ^{230}Th and ^{235}U – ^{231}Pa methods but can also be applied to U–Pb methods.

Introduction

Secondary carbonate precipitates in caves (speleothems) provide an important archive of past environmental conditions (see extensive review in Fairchild and Baker 2012) that can be related directly to past climate and accurately dated by U-series (or U–Th–Pa and U–Pb disequilibrium) methods (Richards and Dorale 2003).

The presence of speleothem deposits is unambiguous evidence that conditions in the karst catchment at the time of formation were suitable for outgassing of carbonate-saturated water; that certain threshold conditions, such as permafrost (e.g., Vaks et al. 2013) or arid conditions (e.g., Wang et al. 2004), did not prevail for significant periods; or that cave passages were not flooded (by rising sea levels or water table, e.g., Richards et al. 1994). Thus, the presence or absence of calcite can be indicative of past climate. Also, successive growth layers in speleothems can preserve geochemical (or proxy) evidence of the state of past climate conditions, and a wide range of variables have been investigated at resolutions from submicron to cm scale, including Mg, Sr, Ba, and U elemental concentrations (e.g., Johnson et al. 2006), molecular organic matter (e.g., Blyth et al. 2008), stable isotopes of O, C (McDermott 2004), Mg (Galy et al. 2002), and Ca (Reynard et al. 2011) in the solid phase and also stable isotopes within fluid inclusions (e.g., Arienzo

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et al. 2013). Particularly important for both geochronology and climatic interpretation is the fact that most vadose speleothems comprise calcite, although not exclusively so, which is a dense, crystalline, stable mineral that is much less susceptible to postdepositional alteration than other climate archives, such as corals, sediments, and shells.

To successfully test models of past climate patterns in both the spatial and temporal domain, we need robust and accurate high-resolution evidence of leads, lags, or synchronous change in proxy climate signals in widely distributed archives. Increased attention on speleothems in the past decade (Henderson 2006) with a motivation to obtain ever higher precision ages on smaller subsamples has demanded constant reassessment of the basic assumptions of this dating technique, that is, accurate assessment of the state of initial conditions, closed-system behavior, and decay constants. Also, for most cases, the determination of axial growth history relies on a subsampling distribution that is less dense for dating than for the climate proxy of interest, which can be as high as sub-annual. For this reason, interpolation and extrapolation methods become just as important, in terms of age precision, as the age determinations themselves.

Initial Conditions

Uranium-series geochronology relies on the extreme fractionation in the hydrosphere of the parent U isotopes (^{238}U , ^{235}U , and ^{234}U) from their long-lived daughters ^{231}Pa and ^{230}Th . Uranium is highly mobile in the meteoric environment as either the uranyl ion or stable carbonate complexes, while the daughter products are readily hydrolyzed and either precipitated or adsorbed on detrital particulates (inorganic or organic), clay minerals, or Fe-oxyhydroxides. Because of these very distinct chemical behaviors in aqueous solutions, precipitation of calcite and other carbonate minerals such as aragonite will incorporate a state of disequilibrium in the ^{238}U and ^{235}U decay chains. With time, the system will evolve toward secular equilibrium (when $^{238}\text{U} \cdot \lambda_{238\text{U}} = ^{234}\text{U} \cdot \lambda_{234\text{U}} = ^{230}\text{Th} \cdot \lambda_{230\text{Th}}$; $^{235}\text{U} \cdot \lambda_{235\text{U}} = ^{231}\text{Pa} \cdot \lambda_{231\text{Pa}}$). With achievable precision for U and Th isotope ratios of sub-permil (<1 ‰) using state-of-the-art multi-collector mass spectrometers, finite ages >500 ka are now routinely possible; however, the maximum possible finite age is dependent on the amount of ^{234}U excess present at time of formation. While ages approaching ~0.8 Ma are possible with current technology, researchers are more likely to turn to alternative techniques including electron spin resonance, paleomagnetism, or U–Pb methods for material of this age and older.

Critical for the U–Th–Pa disequilibrium suite of methods is the assumption of negligible or known concentration of daughter products at the time of formation. It is recognized that there is always a component of Th or Pa adsorbed on detrital clays or colloidal particles, and these can be trapped in the calcite. The extent of detrital, colloidal, or hydrogenous ^{230}Th contamination is estimated by determining the ^{232}Th concentration and correcting for a typical initial $^{230}\text{Th}/^{232}\text{Th}$ activity ratio. For many samples, where silicates and clays are the principal contaminant, a bulk Earth activity ratio of 0.8 ± 0.4 is commonly used. However, this assumption should be tested by using three-dimensional isochron techniques to derive the local initial $^{230}\text{Th}/^{232}\text{Th}$ ratio (Ludwig and Titterton 1994). In numerous settings, radiogenic activity ratio values have been derived, as much as 10–100 times greater than bulk Earth (see Beck et al. 2001; Meckler et al. 2012).

A wide range of U concentrations, perhaps five orders of magnitude, has been observed in groundwaters, and this is reflected in the range of concentrations in secondary carbonate minerals, including speleothems. In general, aragonitic speleothems have higher U concentrations, by virtue of the higher partition coefficient, but calcite speleothems with concentrations $>100 \mu\text{g g}^{-1}$ have

been analyzed. Not surprisingly, higher U concentrations enable smaller sample sizes for the same effective precision. Indeed, researchers are now turning to laser ablation methods, especially in higher-concentration materials, to take advantage of the improved spatial resolution of analysis.

Closed-System Behavior

Speleothems comprise a wide variety of forms and mineralogical compositions; indeed, some samples exhibit repeated shifts in mineralogy associated with changing hydrological and/or climatological conditions. Many subsamples are not suitable for age determination because they exhibit, in section, zones of recrystallization or dissolution fronts. Not all samples provide primary, dense, crystalline calcite or aragonite throughout the growth axis, so the analyst must be careful when selecting specific horizons to date. Occasionally, primary aragonite may be recrystallized to a more stable form of calcite. If this occurs rapidly, the apparent age may be useful (e.g., Frisia et al. 2006). It is expected that material closest to hiatuses in growth might be susceptible to postdepositional alteration, yet this is often the most important calcite because it constrains the timing of initiation or cessation of continuous growth. Also, because sample sizes routinely used for multi-collector ICP-MS measurements are small (<30 mg for material with U concentrations of 100 ng g^{-1}), zones of alteration can easily bias the apparent age. For this reason, dense sampling and duplicate analyses from cogenetic horizons are expected to ensure closed-system behavior of U, Th, and Pa and provide the most accurate determination of the growth histories.

Decay Constants

Uranium-series dating relies on accurate determination of the decay constants involved and is ultimately limited, in terms of precision, by the uncertainties associated with these values. Different strategies have been used to determine these values, the most fundamental of which are direct decay counting or ingrowth. However, a recent update to the decay constants for ^{234}U and ^{230}Th relied on a different strategy (Cheng et al. 2013) that measured the U–Th isotopic ratios in numerous materials that were assumed to be at secular equilibrium and calibrated those measurements against an accurately determined gravimetric standard derived from U and Th metals of known purity. The suite of samples used included speleothems from the Alps, Australia, and South Dakota with ages ranging from 2 to 26 Ma based on U–Pb dating methods and also on vein and mega-crystalline calcite assumed to be much older. Using these improved values for decay constants, age uncertainties of 5–10 ka are achievable for materials older than 500 ka if U concentrations are >1 ppm. This degree of precision is sufficient to test the phasing relationships between records of stable isotopic composition (specifically, $\delta^{18}\text{O}$) in speleothem climate-proxy records and calculations of insolation forcing in the middle Pleistocene (Cheng et al. 2013; see Fig. 1).

Measurement Techniques

Alpha decay counting is still utilized in a few laboratories, but by far the most commonly used platform for analysis is mass spectrometry because of the reduced sample sizes and greater achievable precision. Ionization methods include thermal or inductively coupled plasma (with solution or laser introduction), and a combination of Faraday and ion counters is used for collection

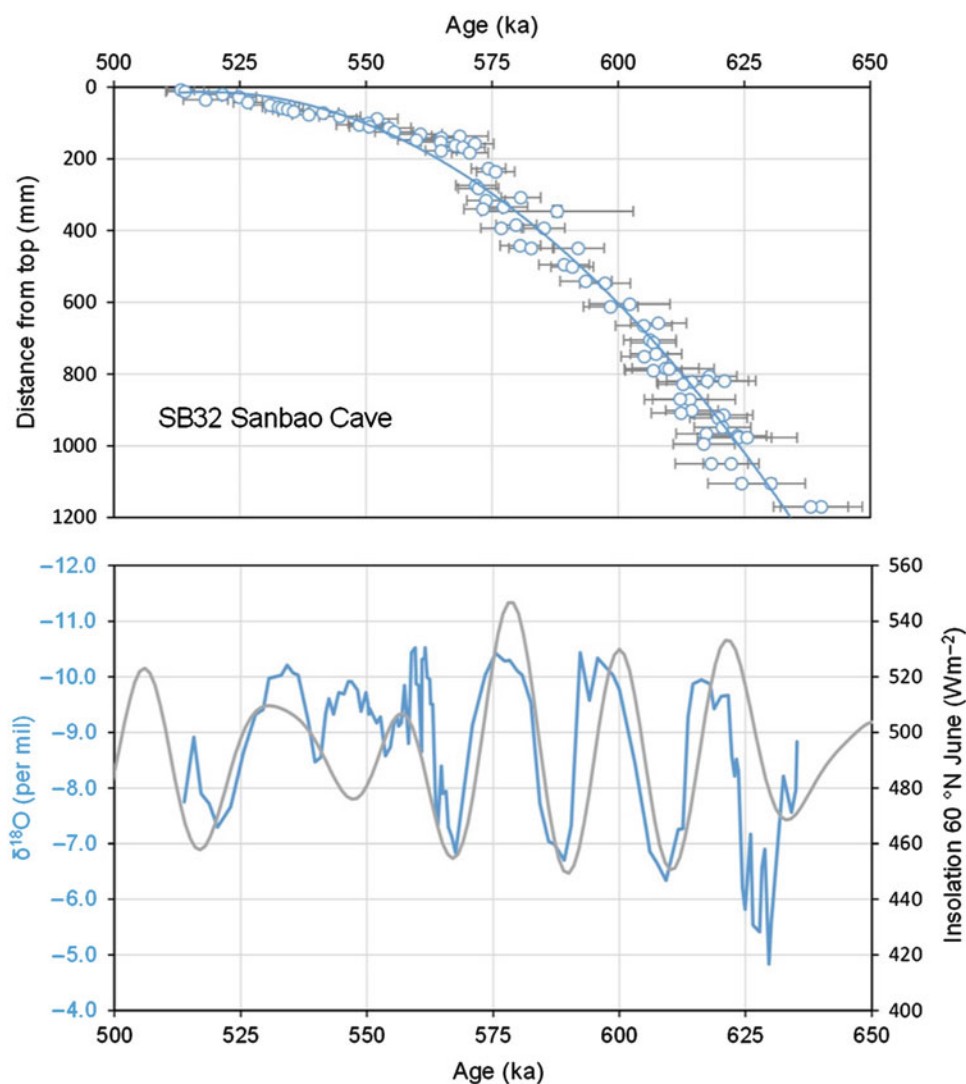


Fig. 1 Sanbao $\delta^{18}\text{O}$ time series, based on the U–Th age–distance relationship using newly determined half-lives (Cheng et al. 2013). The climate-proxy data broadly matches the ~ 23 ka cycles in the summer insolation curve (60° N June, Berger, and Loutre 1991). Routine uncertainties of $< \pm 5$ ka are required to test the phasing of insolation forcing and climate response. Also, the good agreement illustrated is a strong support for the accuracy of the recent determinations of ^{234}U and ^{230}Th half-lives

in static or peak jumping mode, depending on ion beam intensity and required precision. Ionization and transmission efficiency are such that U and Th analysis can be conducted on speleothem subsamples < 50 mg (based on a typical U concentration of 300 ng g^{-1}). U and Th are separated from the carbonate matrix using extraction chromatography or ion-exchange methods prior to mass spectrometric analysis. Age uncertainty is a function of a multitude of parameters including sample size, age, U concentration, beam stability, decay constant uncertainty, and blank contribution.

Laser ablation techniques offer some distinct advantages over solution introduction protocols (see Eggins et al. 2005), although age precisions cannot be matched. If U concentrations are suitable, subsample resolution can be significantly reduced, such that individual domains of $< 100 \mu\text{m}$ can be analyzed. Also, sample preparation is more straightforward (no sample digestion or chemical purification). High-resolution maps of Sr, Ba, Mg, and U based on laser ablation can also reveal the internal architecture of samples, or growth layers, where none were visible petrographically

(Drysdale et al. 2012). These can then guide micro-milling of samples at the submillimeter scale for subsequent high-precision U-series solution work.

Constructing Growth Histories

Chronologies of past climate based on speleothems rely, for the most part, on multiple ages for subsamples that are strategically selected from along the growth axis (see Fig. 1). Subsampling density for the climate proxy of interest is generally at a much greater resolution than that used for dating, and thus, interpolation is required to estimate the age for each lamination formed along the axis. A variety of statistical strategies are employed, including linear interpolation, automatic smoothing splines, Monte Carlo simulation, and Bayesian methodology (for discussion, see Scholz et al. 2012). There is no standard method, and each has advantages and disadvantages with respect to outliers, treatment of hiatuses, and rapid changes in growth rates. Subsamples close to hiatuses are the most susceptible to alteration or contamination because they may have been exposed for extended periods of time; however, they are often the most important because they define the timing of thresholds in local hydrological or climate regime (arid/humid; submergence/emergence). Robust ages have been obtained for submillimeter wafers from former surfaces of flowstones and stalagmites deposited in underwater caves, where the calcite would have been submerged for many thousands of years (see Fig. 2). In spite of the potential problems, many robust chronologies have been developed for terrestrial stalagmite climate-proxy records that match or improve upon the resolutions of records determined from ice and ocean sediment cores, for example.

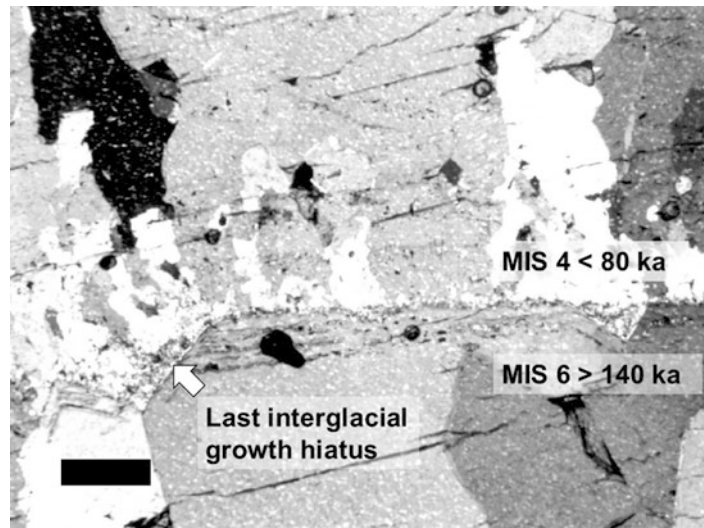


Fig. 2 Hiatus in speleothem flowstone sequence (GB-89-25-5A) collected from 18 m below present sea level in a Bahamas cave (Sagittarius; see Richards et al. 1994). The upper surface of calcite that grew during Marine Isotope 6 (MIS 6; penultimate glaciation >140 ka) was exposed to seawater, freshwater, and air in this inland blue hole prior to reinitiation of growth at ~80 ka. In spite of this, crystal terminations remain well preserved (see *arrow*) and U–Th results show no sign of age inversion (Scale bar, 1 mm width)

Comparison with Other Dating Methods

Ideally, to determine the accuracy of or improve confidence in the constructed growth histories of speleothem climate-proxy records, results determined by U–Th methods should be compared with other dating techniques for the same material. In practice, this is difficult because of the much greater precisions achievable using U-series methods. Radiocarbon methods would be useful in this regard for ages <50 ka (e.g., Hoffmann et al. 2010), but the precisions of ^{14}C dates in carbonates are not comparable because of the variability in dead carbon fraction correction that must be accommodated. Having said this, U–Th dated records (corals and speleothems) play a significant role in calibration of the atmospheric radiocarbon curves, particularly beyond the limit of overlapping tree-ring records (~15 ka). Additional dating methods that can be applied to speleothems include paleomagnetism, electron spin resonance, and Pb-210. Note that U–Pb dating methods can be applied to speleothems and are also included in the suite of disequilibrium methods (see Woodhead et al. 2006).

Conclusions

Uranium-series dating has provided excellent chronological constraints for high-resolution climate, sea level, and permafrost records preserved in secondary carbonates, especially speleothems. These have been compared directly with other climate-proxy records from ice cores, ocean cores, and lake sediments, for example, to test our understanding of the dynamics of past states of the Earth system. Mass spectrometric methods provide sufficient sensitivity to give uncertainties to the nearest year for historical archives and, perhaps, a few thousand years for ages up to ~500 ka. The technique can be applied for as long as a state of radioactive disequilibrium can be distinguished using high-precision analytical techniques on closed-system material and can be extended to include U–Pb methods, which have no effective age limit, if material has relatively high U and low Pb concentrations.

Cross-References

- ▶ [210Pb Dating](#)
- ▶ [Carbonates, Marine \(\$^{14}\text{C}\$ \)](#)
- ▶ [Carbonates, Marine Carbonates, \(U-Series\)](#)
- ▶ [Carbonates, Speleothem Archaeological, \(U-Series\)](#)
- ▶ [Carbonates, Terrestrial \(\$^{14}\text{C}\$ \)](#)
- ▶ [Corals \(Sclerochronology\)](#)
- ▶ [Dendrochronology, Progress](#)
- ▶ [Electron Spin Resonance \(ESR\) Dating, General Principles](#)
- ▶ [Laser Ablation Inductively Coupled Mass Spectrometer \(LA ICP-MS\)](#)
- ▶ [Magnetic Chronology](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Sea-Level Change \(U-Series\)](#)
- ▶ [U-Series Dating](#)

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Carbonates, Pedogenic (U-Series)

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Definition

Pedogenic carbonate: Secondary material consisting of authigenic carbonate and/or silica formed in the shallow vadose zone as part of soil development, typically in arid to semiarid climates.

Geochronological Significance

Pedogenic carbonate, if less than about 0.5 Myr old, dense, and relatively pure, is amenable to uranium-series dating. Such dates can provide useful estimates of the depositional age of the host rock and a time axis for paleoclimate proxy records contained in the carbonate itself.

Origin of Pedogenic Carbonate

Pedogenic carbonate (the term “carbonate” is used here for brevity, but silica is commonly also present either as a dispersed phase or in discrete layers) generally forms in regions with less than 750–1,000 mm annual precipitation, is common in a wide range of climates over more than half of the Earth’s land surface, and generally accumulates most markedly within soil profiles at depths of 0.3–2.0 m (Birkeland 1984). The primary sources of calcium ions (Ca^{2+}) for pedogenic carbonate are detrital carbonate or Ca-bearing silicates present in the parent material, wind-deposited carbonate-bearing dust, and Ca ions in rainwater (Machette 1985; Capo and Chadwick 1999). The latter two sources are sufficient for pedogenic carbonate formation in carbonate-poor parent materials. The requisite carbonate ions (CO_3^{2-}) form in the soil from a complex mixture of atmospheric CO_2 , plant-respired CO_2 , and carbon released by decomposing organic matter (Cerling 1999). The relative contributions of these sources vary with local conditions as revealed by carbon isotope studies (Amundson et al. 1994). During pedogenesis, Ca-bearing minerals are leached from the upper part of the soil profile along with trace amounts of uranium and other elements. At greater depths, typically concentrated between 0.5 and 2 m below the surface, pedogenic carbonate precipitation is caused by increasing ion strength resulting from evaporation, transpiration or freezing, degassing of CO_2 from the soil water, or changing solubility of CaCO_3 as solutions move along temperature gradients in soils (Birkeland 1984). In gravelly soils where substantial pore space may initially surround the sedimentary clasts, carbonate dissolved in the soil solutions is generally precipitated as the consequence of evapotranspiration. In soils as old as a hundred thousand years or more, up to six stages of pedogenic carbonate development have been described (Gile et al. 1966; Machette 1985).

Carbonate-rich clast coatings that begin to form on the bottoms of clasts in the earliest stages of carbonate accumulation in gravelly soils can consist of dense, pure, laminated carbonate that may be

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highly suitable for uranium-series (hereafter, U-series) dating (e.g., Ludwig and Paces 2002; Sharp et al. 2003). Datable thicknesses of such clast coatings (0.5 mm or less) may accumulate in as little as a few hundred years after host deposition. Accordingly, U-series dating of early formed pedogenic carbonate clast coatings can provide useful estimates for the age of gravelly alluvium deposits, which may be otherwise difficult to date.

U-Series Dating Applied to Pedogenic Carbonate

The basis for U-series dating using the $^{230}\text{Th}/\text{U}$ system is derived from the relation among ^{230}Th , ^{234}U and ^{238}U , all nuclides of the ^{238}U decay series. ^{230}Th (half-life 75.69 kyr) is the alpha-decay product of ^{234}U (half-life 245.25 kyr), which in turn forms by alpha decay of ^{238}U (half-life 4.4683 Gyr) through two short-lived intermediate daughter isotopes (Jaffey et al. 1971; Cheng et al. 2000). A closed uranium-bearing system will evolve toward a state of secular equilibrium in which the number of decays per unit time (the activity) of each nuclide in the decay series becomes equal. Newly formed pedogenic carbonate usually contains ppm levels of uranium and is depleted in ^{230}Th relative to secular equilibrium because uranium is immensely more soluble than thorium in oxygenated, infiltrating surface waters and soil waters. The initial concentration of ^{234}U in pedogenic carbonate generally exceeds the value obtained under secular equilibrium conditions because ^{234}U is enriched in soil waters by two processes: (1) ejection from particles by recoil upon its formation by alpha decay from ^{238}U and (2) enhanced solubility relative to ^{238}U because ^{234}U is located in lattice sites damaged by alpha decay. Accordingly, U-series dating using the $^{230}\text{Th}/\text{U}$ system relies on the ingrowth of ^{230}Th and the decay of ^{234}U toward secular equilibrium in a closed system (Ivanovich et al. 1992). Carefully selected, dense pedogenic carbonate has been shown to remain closed with respect to the $^{230}\text{Th}/\text{U}$ system for up to >500 kyr (Ludwig and Paces 2002).

The U-series method is sensitive to the presence of initial ^{230}Th , which will result in anomalously old apparent ages if left uncorrected. Mineralogically pure carbonate precipitated from oxygenated soil waters is likely to have negligible initial Th contents due to its extremely low solubility relative to U. This inference is supported by high $^{230}\text{Th}/^{232}\text{Th}$ activity ratios – that is, the ratio of uranogenic ^{230}Th to common ^{232}Th (the abundant Th isotope, with half-life ~14 Gyr) – observed in some visibly pure pedogenic carbonate samples (e.g., Sharp et al. 2003). These high $^{230}\text{Th}/^{232}\text{Th}$ activity ratios must reflect in situ decay of uranium in initially thorium-poor material (rather than incorporation of extraneous ^{230}Th) because coherent microstratigraphic relations are preserved among subsamples with widely varying $^{230}\text{Th}/^{232}\text{Th}$ ratios. Nonetheless, most pedogenic carbonate contains some ^{232}Th , probably reflecting contamination of the authigenic carbonate cements by fine-grained detritus, implying the presence of detrital ^{230}Th , ^{234}U , and ^{238}U . This detrital component must be subtracted from the measured concentrations to obtain the composition of the pure authigenic component, which has age significance.

U-series dating of pedogenic carbonate was pioneered by Ku et al. (1979), who used 5–8 g samples from the inner 2–3 mm of pedogenic carbonate rinds developed in soils on Pleistocene gravels of the arid Vidal Valley, California. Samples were leached with 1N HCL and both leachates and insoluble residues were analyzed using decay counting by alpha spectrometry. Correction for detrital U and Th isotopes was made using the residue analyses, which had U-Th isotopic ratios close to secular equilibrium and an average atomic $^{232}\text{Th}/^{238}\text{U}$ of 4 – similar to average upper continental crust (Taylor and McLennan 1985). More recently, carefully selected, milligram-size portions of pedogenic carbonate rinds that were totally dissolved and analyzed by mass spectrometry have been shown to be highly suitable for U-series dating (e.g., Ludwig and Paces 2002; Sharp et al. 2003).

Most such samples have sufficiently high $^{230}\text{Th}/^{232}\text{Th}$ activity ratios that correction for initial isotopes can be made using a model detritus composition (Ludwig and Paces 2002). This “single sample, single date” approach precludes meaningless $^{230}\text{Th}/\text{U}$ ages that can sometimes result from chemical fractionation of Th from U during laboratory processing by leach-residue techniques (e.g., Bischoff and Fitzpatrick 1991). Furthermore, the greatly reduced sample size of the latter approach helps to minimize averaging of long ($>10^5$ years), and sometimes visibly discontinuous, depositional histories of individual rinds and allows ages to be tested against microstratigraphic relations.

Highly sensitive analyses of U and Th in carbonates by ICP-MS (inductively coupled mass spectrometry; e.g., Shen et al. 2012) now make it possible to precisely analyze samples of pedogenic carbonate of sub-milligram size. Such analytical improvements, along with laser ablation ICP-MS analyses of carbonates (Hellstrom et al. 2010), facilitate studies of texturally complex, slowly formed pedogenic carbonate microstratigraphic sequences (e.g., Brock and Buck 2005). Where pure pedogenic silica is present, its higher U concentrations (>50 ppm) make analyses by SIMS (secondary ion mass spectrometry; i.e., ion probe) feasible, allowing dating at a spatial resolution of $\sim 30\text{ }\mu\text{m}$, albeit at relatively low precision (age uncertainties of $\pm 10\text{--}20\%$; Maher et al. 2007).

Examples of Application of U-Series Dating to Pedogenic Carbonate

U-series dating of pedogenic carbonate has been used to date landforms offset by faults, thereby establishing the timing and rate of fault motions in Nevada (Ludwig and Paces 2002), Tibet (Blisniuk and Sharp 2003; Gold et al. 2011), and along the San Andreas Fault system in southern California (Fletcher et al. 2010, 2011). Nuriel et al. (2012) studied and dated calcite veins and striations associated with the Dead Sea fault in Israel, thereby constraining the timing of mineralization and related deformation on the fault. Dating of Late Quaternary alluvial fans using U-series on pedogenic carbonate coordinated with ^{10}Be exposure dating has shown that the two techniques provide consistent dates. Combining results from both methods provides enhanced reliability relative to dates determined using a single technique (e.g., Behr et al. 2010; Blisniuk et al. 2012). U-series dating of pedogenic carbonate has been applied to landforms of climatic and geomorphic significance; for example, dates on glaciofluvial terraces in Wyoming help to constrain the timing of the penultimate glaciation in the Rocky Mountains (Sharp et al. 2003). U-series on pedogenic carbonate has been applied to calcic soils in Spain to quantify ages of landforms hosting such soils characterized by advanced stages of pedogenic carbonate development including the formation of calcretes (Candy et al. 2004, 2005).

Summary

Pedogenic carbonate ($\pm$ silica) is widely developed in soils formed in arid to semiarid climates. U-series dating of dense, relatively pure pedogenic carbonate that commonly forms in coarse clastic deposits such as alluvial gravels can provide reliable ages for Middle and Late Quaternary calcic soils and useful estimates of the ages of host deposits and landforms.

Cross-References

- [Carbonates, Lacustrine \(U-series\)](#)
- [Faults \(U-series\)](#)
- [Laser Ablation Inductively Coupled Mass Spectrometry \(LA ICP-MS\)](#)
- [Mass Spectrometry](#)
- [Secondary Ion Mass Spectrometer \(SIMS\)](#)
- [Thermal Ionization Mass Spectrometer \(TIMS\)](#)
- [Uranium Series, Opal](#)
- [U-series Dating](#)

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Chemical Weathering (U-Series)

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Synonyms

[Regolith formation rates](#); [Soil formation rates](#)

Definition

Uranium-series (U-series) isotopes are radionuclides that compose the ^{238}U and ^{235}U decay chains. Measurements of U-series isotopes in soils and river sediments can be used to infer timescales of chemical weathering and derive quantitative estimates of soil age and production rates as well as sediment transport rates through catchments.

Historical Material

U-series isotopes in geological materials have received significant interest since the 1960s (Adams et al. 1959; Pliler and Adams 1962; Cherdyntsev et al. 1964; Rosholt et al. 1966; Syromyatnikov et al. 1967; Hansen and Stout 1968; Scott 1968; Syromyatnikov and Ivanova 1968; Cherdyntsev 1969; Titayeva and Veksler 1977) or even earlier, when investigations were mostly supported by governmental programs motivated by the development of raw materials for nuclear weapons and power (Adams et al. 1959). The first studies were interested with the mobility of actinides in weathering profiles (Pliler and Adams 1962; Rosholt et al. 1966; Hansen and Stout 1968; Hansen and Huntington 1969; Moreira-Nordemann 1977, 1980), while others were investigating the radioactive disequilibrium associated with uranium ore deposits (Cherdyntsev et al. 1964; Syromyatnikov et al. 1967; Lively et al. 1979), in groundwater (Osmond and Cowart 1976, 1982; Cowart and Osmond 1977; Krishnaswami et al. 1982; Osmond et al. 1983) or in streams and estuaries (Scott 1968; Martin et al. 1978; Mangini et al. 1979). Early studies in nuclear physics examined the mechanisms for U-series isotope fractionation (e.g., Linhard and Scharff 1961; Harvey 1962). Later work would explore how these processes could account for radioactive disequilibrium in geological materials with a focus on recoil and preferential leaching effects (Kigoshi 1971; Fleischer and Raabe 1978a, b; Fleischer 1980, 1982a, b, 1983; Sheng and Kuroda 1984; Hussain and Lal 1986; Dran et al. 1988; Adloff and Roessler 1991). Despite a large body of early work on U-series isotope fractionation during chemical weathering, the 1980s and 1990s saw a decrease in interest for this application. However, the topic has regained interest since the late 1990s and early 2000s, in part thanks to improved chemical separation methods (Horwitz et al. 1993; Chabaux et al. 1994; Horwitz 1996; Bourdon et al. 1999) and the development of plasma source

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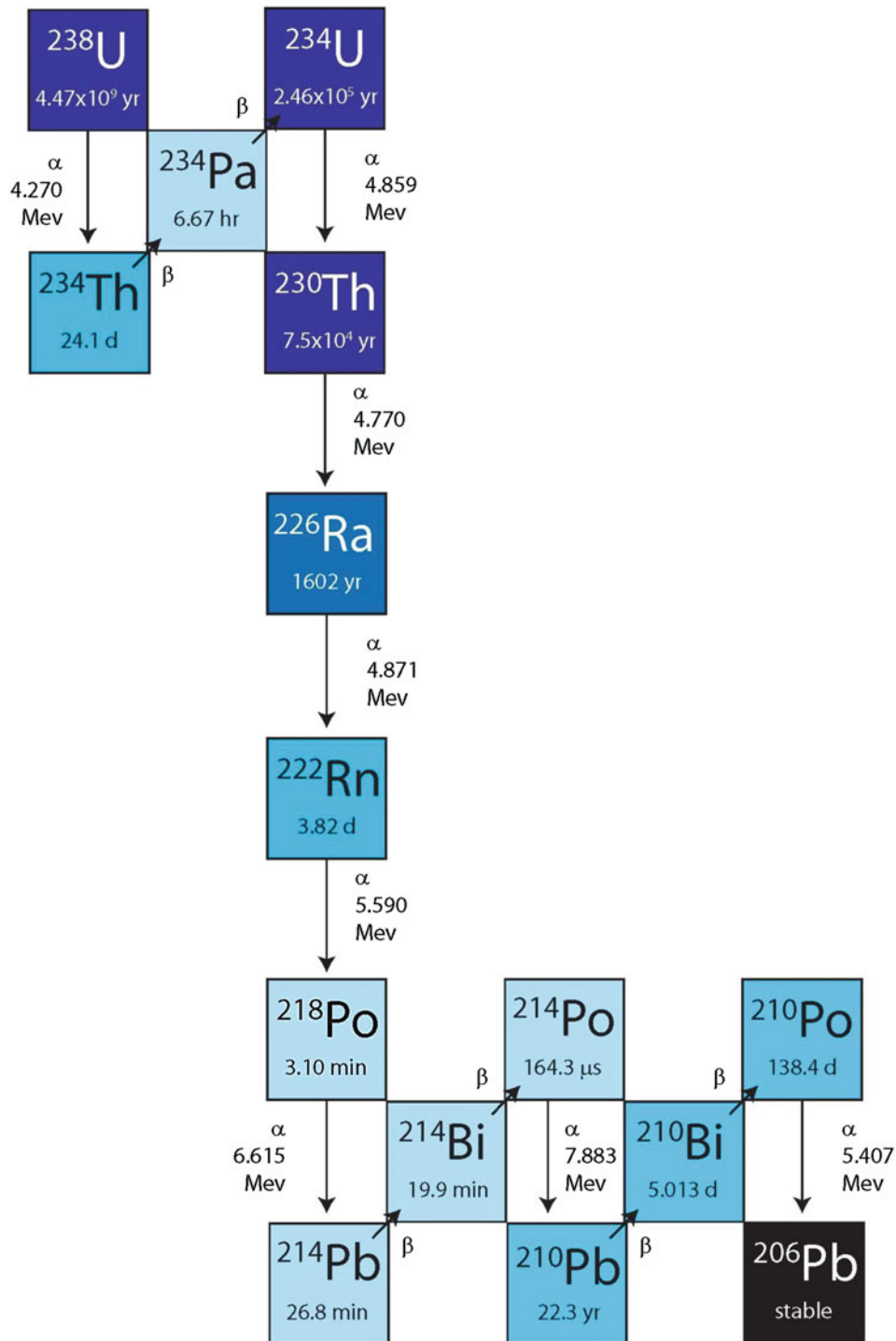


Fig. 1 Uranium-238 decay chain. Each nuclide half-life is shown under its name and expressed in years (yr), days (d), hours (hr), or minutes (min). Two types of radioactive decay occur in the chain: α (decay energy shown under the symbol) and β

mass spectrometry allowing the precise measurement of low abundance U-series isotopes (e.g., Turner et al. 2001).

Essential Concepts and Applications

Uranium-238 (^{238}U) decays through a series of radioactive products to ^{206}Pb as the final, stable isotopic product (Fig. 1). The ^{238}U decay chain is composed of a series of daughter-parent systems where each daughter nuclide is the result of alpha or beta disintegration of the parent nuclide. Although “uranium-series” refer to both ^{238}U and ^{235}U decay chains, most studies focus on the decay products in the ^{238}U decay series, in particular three isotopes: ^{238}U , the parent nuclide of the decay series; ^{234}U , which is produced after alpha decay of ^{238}U into ^{234}Th followed by rapid decays to ^{234}Pa (by beta emission of ^{234}Th with a half-life of 24.1 days) and ^{234}U (by beta emission of ^{234}Pa with a half-life of 6.67 h); and ^{230}Th , produced by alpha decay of ^{234}U with a half-life of 2.46×10^5 a.

For any geological system that remains closed to mass exchange for more than a million years, all radioactive systems in the decay chain are in *secular equilibrium*, i.e., the activity of the daughter nuclide equals that of the parent. The *activity* of a nuclide is its rate of decay, i.e., the product between its abundance and its decay constant. Results are generally expressed in terms of daughter-to-parent activity ratios, for instance, $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$, with the use of parentheses indicating activities. Thus, if a system is in secular equilibrium, these ratios are equal to unity.

A variety of geological processes induce fractionation between U-series isotopes, termed *radioactive disequilibrium*, in which case the activity ratio deviates from unity. Once a disequilibrium is produced, the parent-daughter system will tend to return to secular equilibrium via radioactive decay, over a timescale that is about five times the half-life of the daughter nuclide (for instance, 1.2 Ma for ^{238}U - ^{234}U , 375 ka for ^{234}U - ^{230}Th). Thus, the value of the activity ratio in a geological sample is a function of (i) the behavior of isotopes during geological processes and (ii) the time elapsed since fractionation for a discrete process or the rate of fractionation for a continuous process.

Mechanisms of U-series Disequilibrium

Uranium can be found in two stable oxidation states, 4 and 6, while the only stable oxidation state for thorium is tetravalent. At low oxygen fugacity (i.e., reducing conditions as it is common in the Earth’s interior), uranium is tetravalent and has properties similar to thorium, although differences exist which yield ^{230}Th - ^{238}U disequilibrium in magmas (Harmon and Rosholt 1982; Bourdon et al. 2003; Lundstrom 2003; Turner et al. 2003b; Dosseto et al. 2010). Under oxidizing conditions (as it is commonly the case at the Earth’s surface), U is present in its hexavalent state and forms the uranyl ion UO_2^{2+} . This ion can form stable carbonyl complexes, which accounts for uranium’s solubility in natural waters. In contrast, thorium is relatively insoluble at pH values typical of surface waters (5–8), and it is soluble only in the presence of organic acids at low pH (<3), via binding to organic colloids (Langmuir and Herman 1980; Viers et al. 1997). As a consequence of these chemical behaviors, solutes (e.g., groundwater, soil pore water, and stream water) are generally enriched in U relative to Th and are characterized by $(^{230}\text{Th}/^{238}\text{U})$ activity ratios less than 1. *Weathering products* (hereby restricted to *solid* weathering products, i.e., weathered rocks, soils, stream sediments) are generally enriched in Th relative to U and show $(^{230}\text{Th}/^{238}\text{U})$ activity ratios greater than 1 (Syromyatnikov and Ivanova 1968; Titayeva and Veksler 1977; Latham and Schwarcz 1987).

Although ^{234}U and ^{238}U theoretically have the same chemical behavior, as illustrated by the absence of significant fractionation in igneous rocks, fractionation between these two isotopes occurs at the Earth’s surface, resulting in an enrichment of ^{234}U in natural waters and a depletion in weathered rocks, soils, and sediments (Syromyatnikov and Ivanova 1968; Titayeva and Veksler 1977; Latham and Schwarcz 1987). This fractionation occurs as a consequence of two processes: (i) Direct recoil of ^{234}Th out of the mineral grain during alpha decay of ^{238}U and subsequent beta decays into its granddaughter ^{234}U (Fig. 1; Kigoshi 1971). This occurs because when ^{238}U decays

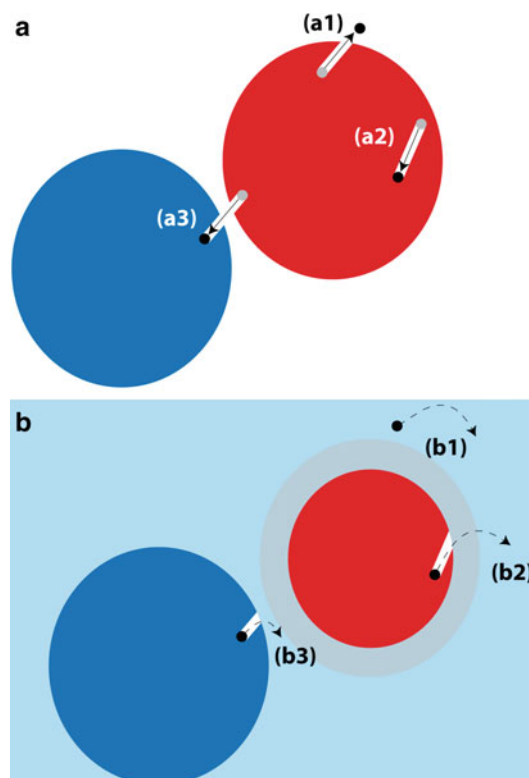


Fig. 2 Schematic representation of various scenarios of alpha decay. In (a), case (a1) occurs when ^{234}Th (black dot) is directly recoiled out of the source mineral (red circle). In case (a2), the direction of recoil from ^{238}U (gray dot) is such that ^{234}Th is embedded further into the source mineral. In case (a3), ^{234}Th is embedded in an adjacent mineral (blue circle). In all cases, ^{234}Th then decays rapidly into ^{234}U . In (b), a fluid fills in the pore space. In case (b1), the ^{234}Th is directly recoiled into the fluid which readily transports the subsequently formed ^{234}U . In case (b2), mineral dissolution (light red area) exposes a recoil track such that the embedded ^{234}U can be leached out of the track. In case (b3), the recoil track in the adjacent mineral is exposed to the fluid and the embedded ^{234}U leached away

into ^{234}Th , the daughter is displaced by 15–35 nm (the *recoil length*) in most minerals (Hashimoto et al. 1985). If this occurs within a recoil length from the mineral surface, a fraction of ^{234}Th can be lost to the surrounding medium (air or water; Fig. 2 case (a1)). (ii) Preferential leaching of ^{234}U embedded in recoil tracks (Fleischer 1980, 1982b). The fraction of recoiled ^{234}Th that is not directly ejected into the surrounding medium is embedded in recoil tracks either deeper the source mineral (Fig. 2 case (a2)) or into adjacent minerals (Fig. 2 case (a3)) especially when the pore space is filled with air (Sun and Furbish 1995). When a solution fills the pore space, the ^{234}U produced by decay is leached out of the exposed recoil tracks in adjacent minerals (Fig. 2 case (b3)) (Fleischer 1980; Andersen et al. 2009) or from newly exposed recoil tracks as a result of dissolution of the source mineral (Fig. 2 case (b2)). Complete leaching of embedded nuclides occurs over a timescale as short as 200 years (Fleischer 1980).

Initially, it was proposed that by determining the fraction of ^{234}Th directly recoiled out of minerals, one could quantify the supply rate of ^{234}U to the solution leaching these minerals (Kigoshi 1971). However, it was later postulated that preferential leaching of embedded ^{234}U is another important mechanism for the delivery of ^{234}U to solutions (Fleischer 1980). It is important to note that although differentiating both mechanisms is important to accurately study the enrichment of solutions in ^{234}U over ^{238}U , when studying the complementary depletion in ^{234}U in residual solids (as it is the case below), such differentiation is not necessary. Indeed, assessments of recoiled ^{234}Th

can overestimate the actual amount of ^{234}U lost to the solution if a significant proportion is embedded into adjacent grains; however, it is exactly because these embedded nuclides are subsequently leached from recoil tracks that eventually all recoiled ^{234}Th end up being lost from the minerals (whether directly recoiled in the water or embedded to another grain and later leached).

As mentioned above, radioactive disequilibrium is generally reported as the ratio of daughter-to-parent activity, e.g., ($^{234}\text{U}/^{238}\text{U}$). The activity ratios used to report U-Th disequilibrium in the literature vary: some studies report ($^{230}\text{Th}/^{234}\text{U}$), while others use ($^{230}\text{Th}/^{238}\text{U}$). Since ^{230}Th is the produce of ^{234}U decay, it would seem more sensible to report ($^{230}\text{Th}/^{234}\text{U}$) ratios. However, if the aim is to study the U-Th disequilibrium imparted by the difference in mobility of U and Th during mineral dissolution, this ratio may not be appropriate: ^{234}U is sensitive not only to U mobilization during dissolution but also to direct recoil and preferential leaching of ^{234}U embedded in recoil tracks. ^{230}Th is also sensitive to these two processes, but because of the high reactivity of Th with particle surfaces, it is highly likely that the ^{230}Th released by recoil or preferential leaching will rapidly re-adsorb on mineral grains. As a consequence, the ($^{230}\text{Th}/^{238}\text{U}$) activity ratio may be a more appropriate measure of the U-Th disequilibrium that occurs during mineral dissolution.

Occurrence of U-series Nuclides in Weathering Products

Weathering products can be simplified as the mixture of four components: (i) primary minerals (i.e., mineral phases from the parent rock), (ii) secondary minerals produced during incongruent dissolution of primary minerals, (iii) secondary minerals produced by precipitation from soil pore water, and (iv) organic matter. Our understanding of the occurrence of U-series disequilibrium is bound to the distribution of U in these components.

As reviewed in Chabaux et al. (2003), uranium can be sorbed onto mineral surfaces with a sorption efficiency ranked as follows: Fe oxides and silica gels > clays and micas > opals (Ames et al. 1983a). For Fe oxides, the sorption efficiency is ordered as follows: amorphous Fe oxyhydroxides > goethite > hematite (Ames et al. 1983a, c; Hsi and Langmuir 1985; Manceau et al. 1992; Waite et al. 1994). For clays, U sorption efficiency is in the following order: montmorillonite > illite > kaolinite (Borovec 1981; Ames et al. 1983a; Shirvington 1983). U can also be sorbed on micas, mostly on muscovite, with a low sorption efficiency for biotite and phlogopite (Ames et al. 1983b). Near-neutral pH conditions tend to favor U sorption, while in acidic conditions, U sorption is enhanced by the presence of humic acids (Lenhart and Honeyman 1999). It has been shown that in some cases, organic acids can control the U budget of weathering products (Plater et al. 1992; Porcelli et al. 1997; Andersson et al. 1998; Dequincey et al. 2002; Chabaux et al. 2003; Vigier et al. 2005; Dosseto et al. 2006a, b). Plater et al. (1992) showed that for bed load sediments from the Witham River in the UK, the organic fraction accounts for 2–12 wt% of the total U budget, while amorphous and crystalline Fe-Mn oxyhydroxides represent 10–20 wt%. They found that resistate minerals, i.e., primary minerals, concentrate 62–85 wt% of the U in the sediments.

In primary minerals, U is mostly found in accessory phases with zircon, xenotime, or monazite exhibiting concentrations as high as several 1,000s of ppm, while ilmenite and magnetite have U concentrations between a few ppm and several 10s of ppm, and apatite between 5 and 150 ppm (Adams et al. 1959). Major minerals like quartz or feldspars contain sub-ppm to ppm levels of U, most likely in liquid inclusions or submicroscopic inclusions of accessory minerals (Adams et al. 1959). Other major minerals like micas or amphiboles can contain up to 10s of ppm of U. Interstitial U, i.e., at grain boundaries, along cleavages, and in microfractures, is another significant pool of uranium in igneous parent rocks (Tieh and Ledger 1981; Guthrie and Kleeman 1986). Guthrie and Kleeman (1986) showed that during the early stages of granite weathering,

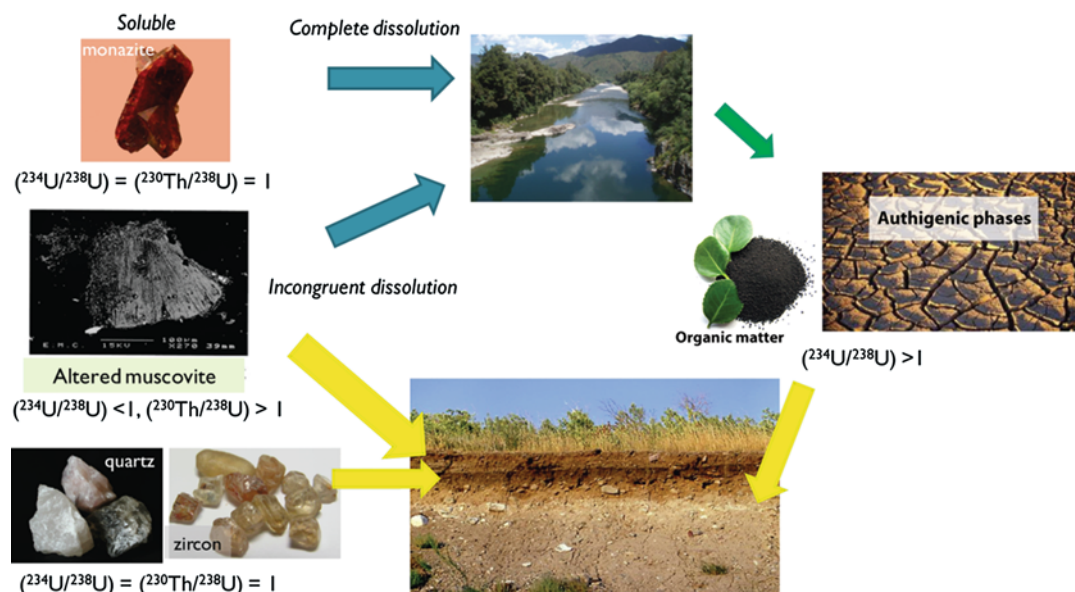


Fig. 3 Schematic representation of the role of the different components of weathering products to their U-series isotope composition. U-poor minerals (e.g., quartz) do not contribute to the radioactive disequilibrium of soils or sediments because of their low U concentration. U-rich minerals that weather readily (e.g., monazite) do not contribute to the radioactive disequilibrium of soils or sediments because they are entirely dissolved and their entire ^{238}U , ^{234}U , and ^{230}Th isotope budget is transferred to the soil-forming solution. Insoluble U-rich minerals (e.g., zircon) do not contribute to radioactive disequilibrium because they are highly resistant to weathering. However, these minerals can contribute to radioactive disequilibrium if (i) they are highly metamict, which favors release of ^{238}U and its decay products, and (ii) they implant ^{234}U and ^{230}Th to adjacent minerals as a result of decay. U-rich primary minerals that weather, but survive weathering (e.g., muscovite or apatite), as well as secondary minerals derived from the incongruent dissolution of these primary minerals provide the dominant control on the U-series isotope composition of soils or sediments. In addition, authigenic phases (as secondary minerals precipitated from soil pore water) and organic matter inherit the U-series isotope composition of the solution from which they formed and can also contribute to the U-series isotope composition of the soil or sediments

“background” U (i.e., contained in quartz and feldspars) is redistributed to the interstitial pool, and a net loss of U occurs via (i) decrease of the interstitial U pool and (ii) dissolution of accessory minerals. While the model abundance of these accessory minerals decreases, their U concentration remains constant.

As shown below, U-series disequilibrium has been used in weathering products to determine the time elapsed since conversion of the parent rock into soils and sediments. In this respect, it is important to note that the behavior of primary minerals during weathering is as important as their U content: to impart radioactive disequilibrium to the weathering product, a mineral must not only (i) contain a significant amount of U but must also (ii) actively dissolve yet (iii) survive chemical weathering. On the one hand, for a U-rich mineral like zircon, because it is highly resistant to chemical weathering, it is likely that no significant loss of nuclides occur via dissolution (Fig. 3). However, it has been shown that intense metamictization can favor zircon weatherability (Balan et al. 2001). Note also that recoil can implant significant amounts of ^{234}U and ^{230}Th to adjacent minerals that may actively dissolve and this can result in a net loss of these nuclides. On the other hand, a U-rich mineral that readily dissolves and is consumed early during weathering will have no contribution to the $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ ratios of the weathering product since all its U-series nuclides will have been lost to the solution (Fig. 3). Thus, the U-series isotope composition of primary minerals and their products is controlled by the U-rich minerals that actively dissolve but

survive the weathering process (Fig. 3). This was recently confirmed by a study of soil profiles in southeastern Australia which found a correlation between the soil residence time inferred from U-series isotopes and the soil muscovite content (Suresh et al. 2011, 2013).

Models of U-series Disequilibrium in Weathering Products

The time-sensitive property of U-series isotopes offers the perspective of being able to determine time constraints on weathering processes. Early studies investigated the qualitative potential of mechanisms to account for observed U-series isotope compositions in soils (e.g., Rosholt et al. 1966; Rosholt 1982). Latham and Schwarcz (1987) and Scott et al. (1992) later developed quantitative models that would describe the evolution of nuclide abundances in weathering products.

In Latham and Schwarcz (1987), a uranium-leach model was proposed to account for ($^{234}\text{U}/^{238}\text{U}$) ≤ 1 and ($^{230}\text{Th}/^{238}\text{U}$) > 1 in weathered granitic rocks. In this model, the abundance of a daughter nuclide, d , in the solid (rock, soil, or sediment) varies with time as a function of the amount of nuclides gained by radioactive decay of the parent, p , and the amount lost by their own decay and via dissolution:

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d - w_d \cdot N_d \quad (1)$$

where N_p and N_d are the number of atoms of the parent and daughter nuclides, respectively; λ_p and λ_d are the decay constants for the parent and daughter nuclides, respectively (in a^{-1}); and w_d is a coefficient that represents the combined loss of the daughter nuclide during mineral dissolution and as a result of recoil when applicable (in a^{-1}). For ^{238}U , the first two terms on the right-hand side are absent because there is no parent, and ^{238}U decay can be neglected over the timescales considered (< 1 Ma).

Scott et al. (1992) proposed a similar weathering model that also explicitly accounts for the loss via recoil of a daughter nuclide produced by α decay.

$$\frac{dN_d}{dt} = (1 - f_d) \lambda_p \cdot N_p - \lambda_d \cdot N_d - w'_d \cdot N_d \quad (2)$$

where f_d is the fraction of daughter nuclide lost by recoil. In this formulation, w'_d is a coefficient that accounts for the loss of daughter nuclide via mineral dissolution only, i.e., if $f_d > 0$, $w'_d < w_d$. Note that for non-radiogenic nuclides (e.g., ^{238}U) or nuclides produced by β decay (e.g., ^{231}Pa), $w' = w$. While ^{234}U is produced by β decay from ^{234}Pa , it is lost by α recoil of ^{234}Th which rapidly decays into ^{234}Pa (half-life, $T_{234\text{Th}} = 24.1$ days), which rapidly decays into ^{234}U ($T_{234\text{Pa}} = 6.09$ h).

It has been proposed that in silt-sized sediments ^{234}U - ^{238}U fractionation occurs mainly via recoil and loss of ^{234}U to the surrounding medium (Maher et al. 2004; DePaolo et al. 2006). In this case, it is assumed that $w'_d = w'_g$ and Eq. (2) can be rearranged to express the ($^{234}\text{U}/^{238}\text{U}$) of the sediment as a function of time:

$$\left(\frac{^{234}\text{U}}{^{238}\text{U}} \right) = \left(\frac{^{234}\text{U}}{^{238}\text{U}} \right)_0 \cdot e^{-\lambda_4 t} + (1 - f_4) \left(1 - e^{-\lambda_4 T_{\text{comm}}} \right) \quad (3)$$

where ($^{234}\text{U}/^{238}\text{U}$)₀ is the initial activity ratio. T_{comm} is termed the comminution age and represents the amount of time needed for the activity ratio to evolve from its initial value (generally the source rock in secular equilibrium) to the observed value in the sediment. Note that because this approach

neglects the effect of chemical weathering (mineral dissolution) on U-series isotope fractionation, it is not discussed further in this contribution. The reader is referred to DePaolo et al. (2012) for a recent review.

Dequincey et al. (1999, 2002) proposed a model that allows not only for the loss of nuclide via mineral dissolution but also for its gain via precipitation of secondary minerals or dust deposition. For instance, the evolution of the abundance of a radiogenic nuclide in the solid is predicted by the equation:

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d + \frac{F_d}{\lambda_d} - w_d \cdot N_d \quad (4)$$

where F_d is the activity input of the daughter nuclide per time unit (in atoms/a²). Note that here, recoil is not explicitly accounted for and is lumped into the dissolution coefficient, as in Latham and Schwarcz (1987).

Dosseto et al. (2008b) later modified this expression and introduced an input coefficient, Γ (in a⁻¹), such that input and dissolution coefficients could be directly compared.

$$\frac{dN_d}{dt} = \lambda_p \cdot N_p - \lambda_d \cdot N_d + \Gamma_d N_{d,i} - w_d \cdot N_d \quad (5)$$

The input coefficient Γ_d reflects how fast the initial concentration $N_{d,i}$ is increased by nuclide addition. Thus, the term $\Gamma_d N_{d,i}$ represents the flux of added nuclides (in atoms/g/a). Note that the model is sensitive to the initial isotopic ratios but not to the initial isotopic abundances (i.e., the initial U concentration, $N_{d,i}$, does not impact calculated activity ratios, but the initial activity ratios obviously do).

In order to better understand the evolution of each nuclide's abundance in the solid according to these models, processes that affect the mobility of each nuclide are reviewed below.

Mobility of ²³⁸U:

- Loss during mineral dissolution, releasing ²³⁸U to the solution (coefficient w_8). The ability of ²³⁸U to stay in solution then depends of the redox conditions, as explained above: in reducing conditions, tetravalent ²³⁸U has low solubility and will precipitate out of the solution, while in oxidizing conditions (typical of near-surface environments where mineral dissolution by weathering takes place), ²³⁸U will form the uranyl ion ²³⁸UO₂²⁺ which readily complexes with the carbonate ion to create a very stable and highly soluble species.
- Sorption from soil pore water onto mineral surfaces (coefficient Γ_8). It has been shown that uranium can be easily adsorbed on micas, clays, iron oxyhydroxides, and organic matter (Ames et al. 1983a, b, c; Chabaux et al. 2003), with a sorption capacity ranking as follows: hydrous Fe oxides > well-crystallized goethite >> montmorillonite > kaolinite (Szalay 1964; Manceau et al. 1992). Because sorption is enhanced by greater surface areas, this process has been invoked to account for the increasing radionuclide concentrations with decreasing grain size in soils (Megumi and Mamuro 1977).
- Precipitation of authigenic phases (coefficient Γ_8). The formation of carbonates and Fe-Mn oxyhydroxides can scavenge significant amounts of U from solution where U will be either adsorbed onto surfaces (see above) or incorporated into the crystal structure by isomorphic substitution (see review in Chabaux et al. 2003). When considering bulk soils or stream

sediments, the ^{238}U in these secondary phases can represent a significant proportion of the ^{238}U budget (e.g., Plater et al. 1992).

- Dust deposition (coefficient Γ_8). Gain of ^{238}U can also occur via deposition of mineral aerosols. Pett-Ridge et al. (2007) attributed U enrichments up to 531 % in Hawaiian soils older than 150 ka by dust deposition. Pelt et al. (2013) showed that dust deposition can account for up to 25 % of the U and Th budget of basaltic soils in Cameroon. Note that these are extreme scenarios because the parent material (basalt) has a low U content. The contributions from dust to the soil U budget would be less significant in granitic and sedimentary environments. Nevertheless, gain of ^{238}U via dust deposition is accounted for in the model by the parameter Γ_8 .

It is important to note that the numerical models only account for the gain of ^{238}U without differentiating between the different processes of sorption, precipitation, or dust deposition that contribute to that gain.

Mobility of ^{234}U :

- Loss during mineral dissolution (coefficient w_4). Congruent dissolution will release ^{234}U at the same rate as ^{238}U (not taking into account the preferential leaching mentioned below). In this case, no fractionation between these isotopes is expected, i.e., $w_4 = w_8$.
- Direct recoil of ^{234}Th and subsequent decay into ^{234}U contributes to enhance ^{234}U mobility compared to ^{238}U . The fraction ^{234}U lost by recoil in Scott et al.'s model is $1 - f_4$.
- Preferential leaching of ^{234}U embedded in recoil tracks. Tracks can provide pathways for migrating solutions to reach ^{234}U , thereby enhancing the mobility of ^{234}U compared to undecayed ^{238}U , i.e., $w_4 > w_8$.
- Preferential oxidation of ^{234}U compared to ^{238}U . Computer simulations of the recoiled ^{234}Th motion have shown that in minerals with a low U content, there is a high probability for ^{234}U to be found in the vicinity of oxygen atoms or radicals, making it more prone to oxidation to the hexavalent state resulting in preferential mobilization compared to tetravalent ^{238}U (Adloff and Roessler 1991). This will also contribute to a coefficient w_4 greater than w_8 .
- Sorption of ^{234}U on mineral phases (coefficient Γ_4). Although untested, it is believed that no fractionation between ^{234}U and ^{238}U occurs during this process. Thus, the adsorbed U will record the ($^{234}\text{U}/^{238}\text{U}$) ratio of the solution (i.e., Γ_4/Γ_8), which in most cases will be greater than 1. This relation is supported by measurements of ($^{234}\text{U}/^{238}\text{U}$) ratios in the exchangeable fraction leached from organic matter, carbonates, and crystalline Fe-Mn oxides that were bound to river sediments: all leachates showed values within analytical error of 1.3 (Plater et al. 1992).
- Precipitation of authigenic phases (coefficient Γ_4). As with ^{238}U , ^{234}U can be added to the bulk soil or stream sediment during the precipitation of secondary phases. Because no fractionation between ^{234}U and ^{238}U is believed to occur during secondary mineral precipitation, U in the precipitated phases will record the ($^{234}\text{U}/^{238}\text{U}$) ratio of the solution (in most cases greater than 1), which will define values of Γ_4/Γ_8 .
- Dust deposition (coefficient Γ_4). Similarly to ^{238}U , gain of ^{234}U can occur via the deposition of mineral aerosol. If this is a substantive process for U gain, the Γ_4/Γ_8 ratio represents the ($^{234}\text{U}/^{238}\text{U}$) activity ratio of the dust component.

Considering the processes described above, if sorbed U and authigenic phases can be removed by sequential leaching, we should observe ($^{234}\text{U}/^{238}\text{U}$) activity ratios <1 in weathering products. However, this is not always the case (Lee et al. 2010). A ($^{234}\text{U}/^{238}\text{U}$) >1 could be explained by the Sheng-Kuroda effect (Sheng and Kuroda 1986a, b). In this case, U-poor residual minerals can be

enriched in ^{234}U by implantation from U-rich minerals, which are subsequently removed by dissolution. Note that this process excludes zircon as a source for ^{234}U implantation as it is highly resilient to weathering.

Mobility of ^{230}Th :

- Loss during mineral dissolution (coefficient w_0). As ^{230}Th is produced by alpha decay of ^{234}U , it will be located in recoil tracks. Thus, as the mineral dissolves, recoil tracks will be exposed to migrating solutions allowing release of ^{230}Th . However, Th is highly insoluble, and any Th released to the solution is likely to precipitate back and/or be adsorbed on residual minerals. For these reasons, in most studies, it is assumed that $w_0 \ll w_4$ or w_8 . Nevertheless, significant ^{230}Th solubilization can occur in the presence of organic acids and colloids and/or at low pH (Langmuir and Herman 1980; Viers et al. 1997; Chabaux et al. 2003; Dosseto et al. 2006a, b). For instance, sediments from organic-rich rivers of the Amazon basin are characterized by $(^{230}\text{Th}/^{238}\text{U}) < 1$ (Dosseto et al. 2006a).
- Direct recoil of ^{230}Th during decay of ^{234}U . If decay of ^{234}U occurs within a few tens of nm of the mineral surface, ^{230}Th can be recoiled out of the mineral into the surrounding medium (air or water). The fraction of ^{230}Th lost by recoil is $1 - f_0$. However, as explained above, because of Th low solubility and its high reactivity for mineral surfaces (especially Fe-Mn oxyhydroxides), it is likely that ^{230}Th will be rapidly re-adsorbed onto mineral surfaces.
- Sorption of ^{230}Th from the solution onto minerals or incorporation into secondary minerals (coefficient Γ_0). Th can sorb onto organic matter, clays, and Fe-Mn oxyhydroxides (Chabaux et al. 2003), resulting in a gain of ^{230}Th . Based on $(^{230}\text{Th}/^{238}\text{U})$ and $(^{230}\text{Th}/^{234}\text{U})$ activity ratios measured during sequential leaching experiments of river sediments (Plater et al. 1992), it appears that U has a higher affinity for organic matter than Th (thus, Γ_8 or $\Gamma_4 > \Gamma_0$), while the opposite is observed for Fe-Mn oxides ($\Gamma_0 > \Gamma_8$ or Γ_4).
- Dust deposition (coefficient Γ_0). Gain of ^{230}Th can also occur via deposition of mineral aerosols. If this is a substantive process for the gain of U and Th isotopes, then the Γ_0/Γ_8 ratio reflects the $(^{230}\text{Th}/^{238}\text{U})$ activity ratio of the dust component (expected to be greater than 1).

Hence, based on the processes described above, $(^{230}\text{Th}/^{238}\text{U})$ ratios $>$ or < 1 can be observed in weathering products. Because $(^{230}\text{Th}/^{238}\text{U}) > 1$ are more commonly observed, it is likely that conditions where ^{230}Th is insoluble, or where any ^{230}Th lost via recoil is adsorbed onto Fe-Mn oxides, generally prevail.

A corollary from these observations is that at low dissolution rates, and where sorbed nuclides and secondary minerals have been removed, recoil of ^{230}Th should become important and $(^{230}\text{Th}/^{238}\text{U}) < 1$ should be expected in solids. This is similar to what has been proposed to explain $(^{234}\text{U}/^{238}\text{U})$ in waters from New Zealand (Robinson et al. 2004), where loss of ^{234}U is enhanced in situations where physical weathering (comminution) dominates over chemical weathering, thus favoring recoiled ^{234}U over the bulk loss of U.

The concepts and models presented above are used to describe how $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ ratios evolve from initial to observed sets of values over a period of time. The initial $(^{234}\text{U}/^{238}\text{U})$ and $(^{230}\text{Th}/^{238}\text{U})$ are generally taken as those of the parent rock and assumed to represent secular equilibrium (i.e., all U-series activity ratios are equal to 1). Alternatively, when modeling regolith compositions in a weathering profile, initial ratios can be those of a deeper regolith sample. The amount of time required to evolve from initial to observed isotopic compositions represents the *duration of weathering*. In a weathering profile, this can be equivalent to the age of the weathering front, termed *weathering age*, i.e., the time elapsed since the weathering front was at a given depth

(Dosseto et al. 2008b, 2012). In river sediments, this is equivalent to the *residence time of sediments in the catchment*, i.e., the time spent by sediments in the catchment since production from the bedrock, integrating storage in weathering profiles and transport in the river (Chabaux et al. 2008; Dosseto et al. 2008a; Vigier and Bourdon 2011).

The set of parameters that best describe the observed ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$) ratios is sought for, generally by inverse modeling. The resulting parameters derived from the models are the duration of weathering and the set of coefficients for each nuclide (depending on the models: f_i , w_i , and/or Γ_i , where i is the nuclide considered).

To solve these models, several important assumptions are required:

1. The coefficients for nuclide loss, w , and gain, Γ , are constant over the duration of weathering. This assumption is commonly made in studies that model chemical weathering (e.g., Chamberlain et al. 2005; Ferrier and Kirchner 2008) and laboratory experiments that suggest constant w values for a given mineral (White and Brantley 2003).
2. In Scott et al.'s (1992) model, the fraction of recoiled nuclides (coefficient f) is constant over the duration of weathering.
3. Nuclide loss and gain operate on similar timescales.
4. Because of the large number of unknowns, several samples are required, and it is assumed that their activity ratios differ only as a result of different durations of weathering. Hence, each coefficient for each nuclide is assumed to be constant across samples.

These assumptions are difficult to verify because (1) conditions for mineral dissolution and precipitation are variable with time, especially over the timescales typically modeled (10^3 – 10^6 years). It is generally assumed that any actual variations will average out over such long timescales. (2) The fraction of recoiled nuclide is dependent on the surface properties of the material, which may vary with time (e.g., as the result of mineral dissolution). (3) The onset of nuclide loss (weathering) could take place significantly earlier than nuclide gain (e.g., illuviation). Nevertheless, even in the early stages of weathering, secondary minerals that contain significant amounts of U are observed (Guthrie and Kleeman 1986; Pelt et al. 2008). (4) Constant nuclide gain and loss coefficients between samples are difficult to verify because conditions of mineral dissolution and precipitation can be variable even over small length scales. Despite these strong caveats, previous studies have yielded unprecedented constraints on rates of soil formation and sediment transport (see Chabaux et al. 2008; Dosseto et al. 2008a; Vigier and Bourdon 2011 for recent reviews).

Current Investigations, Controversies, and Gaps in Knowledge

This section presents a review of studies using U-series isotopes to constrain timescales of chemical weathering in weathering profiles, rinds, and soil chronosequences. For a review of applications to fluvial sediments, the reader is referred to the reviews by Dosseto et al. (2008a) and DePaolo et al. (2012).

Weathering Profiles

When discussing weathering profiles, we must first define a few terms. Here, the *soil* is defined as the top part of the weathering profile, which is mobile as it creeps downhill (colluvial transport). Soil production occurs by physical and chemical weathering of the underlying saprolite or bedrock, often with living organisms playing a preponderant role. The *saprolite* is defined as weathered material

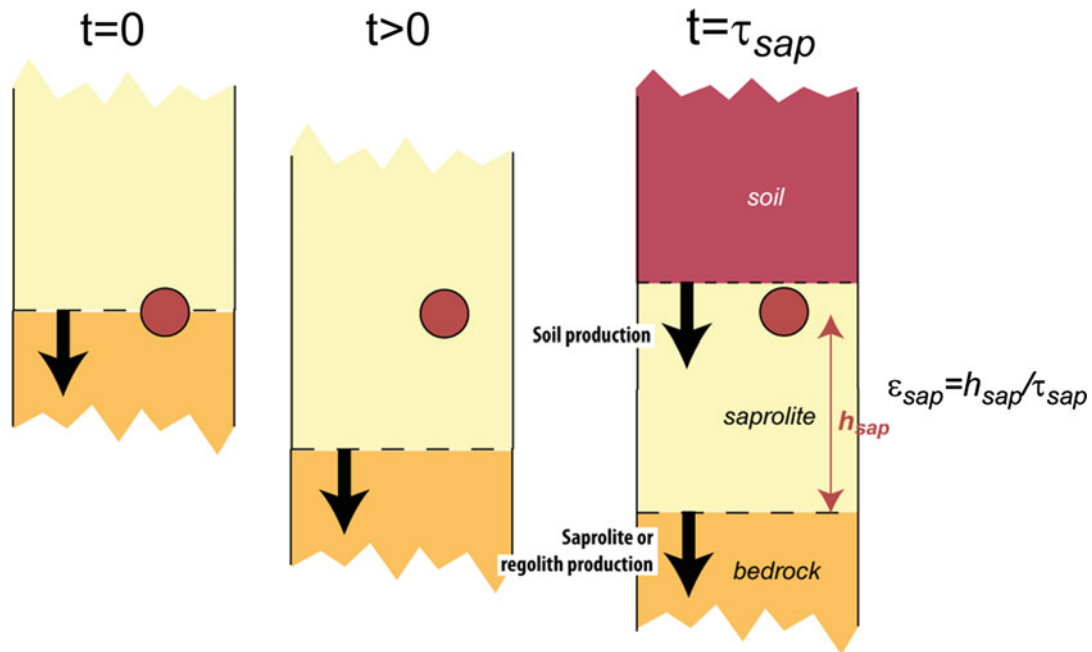


Fig. 4 Conceptual definitions of the *weathering age* and the *sapolite/regolith production rate*. If one considers the downward propagation of the weathering front into bedrock (*lower dashed line*), the weathering age, τ_{sap} , of a given sapolite sample (*red dot*) is the amount of time required for the weathering front to migrate over the distance h_{sap} , which is the height of the sample above the current weathering front. The sapolite or regolith production rate ϵ_{sap} (in mm/ka), averaged over the distance h_{sap} , can then be calculated by dividing h_{sap} (in mm) by τ_{sap} (in ka) (Modified from Dosseto et al. (2008b))

that still retains some structural aspects of the bedrock. It is produced at the *weathering front* by physical and chemical weathering of the bedrock. The *regolith* is the ensemble of sapolite and soil, which together constitutes the *weathering profile*. Thus, sapolite production, regolith production, and weathering front advance refer to the same process.

The development of weathering profiles is the result of a complex interaction between tectonics, climatic, and biotic processes. The thickness and nature of these profiles are an expression of landscape evolution in response to these various mechanisms. The topsoil is of particular importance because it is the basic resource required for sustaining nearly all biological ecosystems including agriculture and human civilizations. Despite this importance, little is known on how fast weathering profiles develop. In contrast, their rate of denudation is well constrained, even at millennial timescales (using cosmogenic isotopes; Brown et al. 1995, 1998). Cosmogenic isotopes can also be used to determine soil production rates (Heimsath et al. 1997; Larsen et al. 2014); however, this requires the assumption that the soil thickness is in steady state, which is seldom verifiable. This approach, by definition, renders it impossible to evaluate soil evolution, i.e., imbalances between production and denudation. Indeed, even if soil thickness has reached a steady state, how was it achieved? The soil must have been thickening before reaching steady state. Furthermore, soil production is only one aspect of the development of a weathering profile, with production of sapolite or regolith being the other, even more important aspect. It has been proposed that cosmogenic isotopes could also be used to infer sapolite production rates (Dixon et al. 2009); however, this suggestion also requires the assumption that the entire weathering profile thickness is in steady state, which is not easily tested.

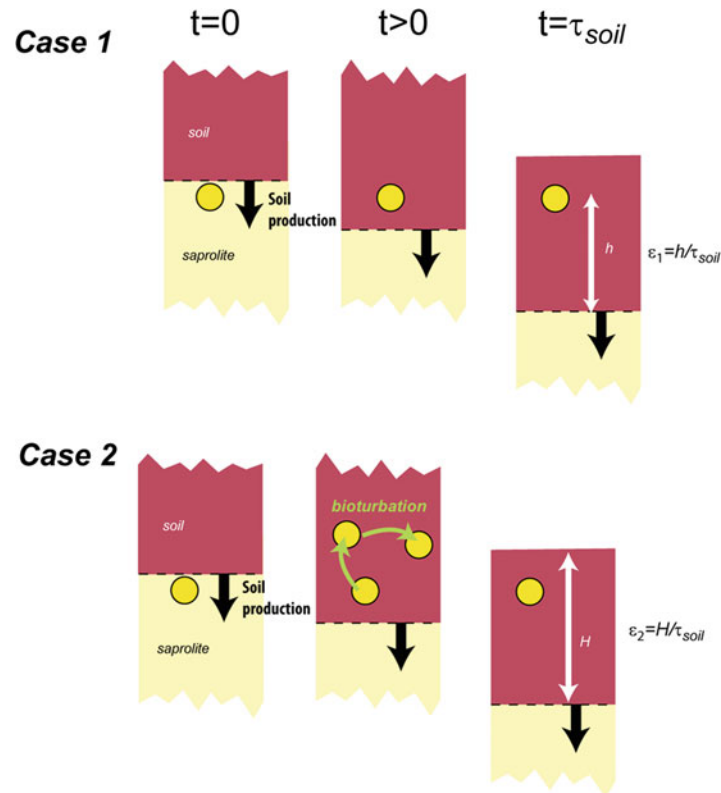


Fig. 5 Conceptual definitions of the *soil weathering age* and *production rate*. If one considers a given soil sample (yellow dot), the soil weathering age, τ_{soil} , is the amount of time required for the soil-saprolite boundary (dashed line) to migrate downward over the distance h . The distance h represents the height of the soil sample above the current soil-saprolite boundary. Two cases are considered: in case 1, bioturbation is neglected, and the soil production rate ϵ_1 , averaged over the distance h , is the ratio of h over τ_{soil} . In case 2, bioturbation is considered, and the soil production rate ϵ_2 , averaged over the entire soil thickness H , is the ratio of H over τ_{soil} . In the latter case, the soil thickness must be in steady state in order to obtain a meaningful production rate (Modified from Dosseto et al. (2008b))

U-series isotopes offer an alternative to quantify soil and saprolite production rates. Using the model of Dequincey et al. (2002), it is possible to model the amount of time that elapsed to produce the observed U-series isotope composition since departure from secular equilibrium. This is equivalent to the time elapsed since the onset of chemical weathering and is termed *weathering age* (Fig. 4). By using the weathering age of a given saprolite sample in the profile and its height above the weathering front (i.e., the difference between its depth and the depth of the weathering front), we can infer an average saprolite (or regolith) production rate. This represents the average rate at which the weathering front has propagated between the two depths considered (Fig. 4). Similarly, considering a soil sample and using the composition of the underlying saprolite as the initial conditions, we can use the time required to evolve from the U-series isotope composition of the saprolite to that of the soil sample and the height of the soil sample above the soil-saprolite boundary to infer an average soil production rate (Fig. 5).

This approach has been applied to weathering profiles developed over granitic lithologies in tectonically passive, tropical/equatorial regions of south America (Mathieu et al. 1995) and western Africa (Boulad et al. 1977; Dequincey et al. 1999, 2002). In Cameroon, Boulad et al. (1977) estimated regolith production rates of 70 mm/ka (Fig. 6 and Table 2). In Burkina Faso, while no regolith production rate was estimated, Dequincey et al. (2002) determined weathering ages of ~400–500 ka. In the Amazon, Mathieu et al. (1995) calculated that it took ~300 ka to develop 15 m

Table 1 Parameters used for U-series isotope models

Parameter	Description	Units
N_8, N_4, N_0	Concentrations of ^{238}U , ^{234}U , and ^{230}Th , respectively	Atoms g^{-1}
$\lambda_8, \lambda_4, \lambda_0$	Decay constants for ^{238}U , ^{234}U , and ^{230}Th , respectively	a^{-1}
w_8, w_4, w_0	Dissolution coefficients for ^{238}U , ^{234}U , and ^{230}Th , respectively	a^{-1}
$\Gamma_8, \Gamma_4, \Gamma_0$	Gain coefficients for ^{238}U , ^{234}U , and ^{230}Th , respectively	a^{-1}
f_4, f_0	Fraction of recoiled ^{234}Th (and thus ^{234}U) and ^{230}Th , respectively	Unitless

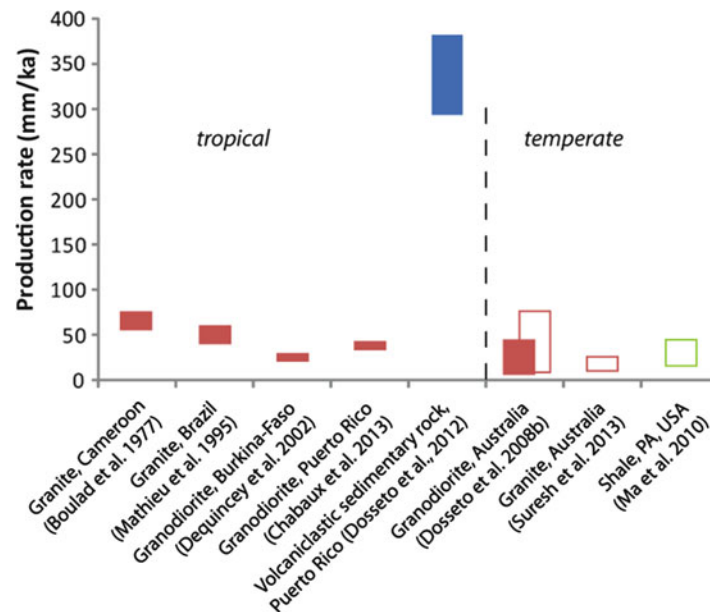


Fig. 6 Compilation of U-series-isotope-derived regolith (closed *rectangles*) and soil (*open rectangles*) production rates (in mm/ka)

of regolith in the Amazon. This implies an average regolith production rate of 50 mm/ka (Table 2). These production rates are surprisingly high considering that (i) erosion rates in these areas are most likely <10 mm/ka and (ii) weathering rates are expected to be slow because the weathering front is several tens of meters deep and likely to be isolated from meteoric waters (Gaillardet et al. 1995, 1997, 1999). However, it is important to note that regolith production rates inferred from U-series isotopes are averaged over a timescale that represents the weathering age. Thus while modern weathering rates are most likely slow, they were probably much higher in the past when the weathering front was closer to the surface and subject to higher rainfall and temperatures.

A U-series isotope study was also conducted in Puerto Rico (Chabaux et al. 2013), where the weathering profile is also developed over a granitic parent rock under tropical conditions, but erosion rates are much higher than in western Africa or Brazil (43 ± 15 mm/ka (Brown et al. 1995); 33 ± 8 mm/ka (Riebe et al. 2003)). Calculated regolith production rates were 45 ± 12 mm/ka (Chabaux et al. 2013) (Table 2). This implies that, at the scale of the weathering profile, the loss of regolith is largely balanced by its production from the bedrock. A recent U-series study of stream sediments in the same area shows that a balance between rates of regolith production and erosion is also true at the catchment scale (Dosseto et al. 2014). These results are in agreement with previous work (White et al. 1998; Riebe et al. 2003; Turner et al. 2003a; Pett-Ridge et al. 2009a, b; Ferrier et al. 2010). Furthermore, similar regolith production rates over granitic parent rock in

Table 2 Compilation of regolith and soil production rates from U-series isotope studies

Location	Parent rock	Regolith (or saprolite) production rate (mm/ka)	Soil production rate (mm/ka)	Reference
<i>Weathering profiles</i>				
Cameroon	Granite	70	n/d	Boulad et al. (1977)
Burkina Faso	Granodiorite	30–40	n/d	Dequincey et al. (2002)
Amazon (Brazil)	Granite	50	n/d	Mathieu et al. (1995)
Icacos (Puerto Rico)	Granodiorite	45 ± 12	n/d	Chabaux et al. (2013)
Bisley (Puerto Rico)	Volcaniclastic sedimentary rock	334 ± 46	n/d	Dosseto et al. (2012)
Nunnock (Australia)	Granodiorite	4–46	12–77	Dosseto et al. (2008b)
Frogs Hollow (Australia)	Granite	n/d	10–24	Suresh et al. (2013)
Shale Hills (PA, USA)	Shale	n/d	17–50	Ma et al. (2010, 2013)
<i>Weathering rinds</i>		Rind formation rate (mm/ka)		
Costa Rica	Basalt	0.5 ± 0.2		Pelt et al. (2008)
Guadeloupe	Basalt	0.18–0.24		Ma et al. (2012)
Icacos (Puerto Rico)	Granodiorite	52 ± 13		Chabaux et al. (2013)

different areas suggest that production is relatively insensitive to erosion rates and is mostly controlled by the composition of the parent rock and/or climatic conditions.

Dosseto et al. (2012) suggested that the composition of the parent rock is a more important control on regolith production rates than climatic conditions, because they calculated production rates of 334 ± 46 mm/ka for a weathering profile developed over a volcaniclastic sedimentary rock in the same region (and thus very similar climatic conditions) as the granitic profile of Chabaux et al. (2013) (Fig. 6 and Table 2). These rates are faster than those for the granitic profile by a factor of ~ 4 .

Studies have also been conducted in temperate regions for weathering profiles developed over granitic lithologies in southeastern Australia (Dosseto et al. 2008b; Suresh et al. 2013) and shale in northeastern USA (Ma et al. 2010, 2012). In southeastern Australia, the region studied is characterized by a retreating escarpment separating a coastal plain to the east from highland plateaus (elevation ~ 900 m) to the west. Weathering profiles were studied in two different geomorphic contexts: on the escarpment (Dosseto et al. 2008b) and on the plateau (Suresh et al. 2013). Sampling strategies differed between the two studies in that Dosseto et al. (2008b) sampled profiles across the hillslope, while Suresh et al. (2013) sampled profiles on ridgetops so that colluvial transport could be neglected.

On the escarpment, saprolite weathering ages ranged from 0.55 to 6.2 Ma. Values increase downhill with distance from the ridge. These estimates represent the amount of time required to develop ~ 25 m of saprolite and result in saprolite production rates ranging between 4 and 46 mm/ka (Dosseto et al. 2008b) (Table 2). These values are similar to local estimates of denudation rates

(9–68 mm/ka; Heimsath et al. 2000), thus demonstrating that the entire weathering profile is in steady state. This suggests that, over the 0.55–6.2 Ma of saprolite development, an equilibrium has been reached between erosion and the conversion of granitic bedrock into saprolite. Similarly, soil weathering ages range from 6 to 38 ka representing the amount of time needed to develop ~0.5–1 m of soil from the underlying saprolite. Soil production rates calculated from U-series range from 12 to 77 mm/ka (Table 2). Here again, it is similar to denudation rates and demonstrates that the soil thickness is in steady state too. Thus, at this site, the three major interfaces that constitute the weathering profile (atmosphere-soil, soil-saprolite, and saprolite-rock) are progressing downward at similar rates. These results are surprising as the escarpment is the most dynamic part of the landscape in this region.

On the plateau, calculated soil weathering ages are up to 30 ka. This represents the amount of time required to develop 30–60 cm of soil from the saprolite. Soil production rates show a much narrower range than at the escarpment, between 10 and 24 mm/ka (Suresh et al. 2013) (Table 2). Here too, production rates are similar to denudation rates inferred from cosmogenic isotopes, effectively demonstrating that soil thickness has also reached a steady state.

At the Susquehanna/Shale Hills Critical Zone Observatory in northeastern USA, Ma et al. (2010, 2013) quantified soil weathering ages and production rates from pits along two opposing hillslopes, developed over a Palaeozoic shale. On the north-facing hillslope, soil weathering ages vary between 7 and 40 ka, representing the amount of time to develop 30–70 cm of soil. This amounts to soil production rates of 17–45 mm/ka (Ma et al. 2010) (Table 2). On the south-facing hillslope, soil weathering ages vary between 12 and 16 ka (to develop 60–80 cm of soil). Inferred soil production rates are 40–50 mm/ka (Ma et al. 2013) (Table 2). These rates are similar to the range observed in granitic environments. This suggests that the composition of the parent rock has little effect on the rate of soil production. However, in the case of Shale Hills, the soil is directly developed over the parent rock, while in granitic environments it is developed over a saprolite. It is thus difficult to use results from the Shale Hills site to assess the role of parent rock composition since pedogenetic processes are quite different from those related to weathering profiles developed over granitic or volcanoclastic sedimentary parent rock.

Soil Chronosequences

Soil chronosequences are defined as a group of soils that differ in age but have similar parent materials and have formed under similar conditions of climate, vegetation, and geomorphic position (Jenny 1941). They are particularly useful for U-series isotopic studies if the soil's maximum weathering age is known as they can then be used to calibrate the U-series isotope weathering models.

Pett-Ridge et al. (2007) have studied a chronosequence of soils developed in Hawaiian tephras with ages ranging from 0.3 to 4,100 ka. They showed that the U budget of the soil is largely dominated by dust deposition at older sites and that Fe oxides are the main mineral phases carrying U in these soils. Pelt et al. (2013) reached similar conclusions on the role of dust deposition on the U budget of soils in a study of Holocene basaltic flows in Cameroon. These results are a consequence of rapid dissolution of primary phases in basaltic parental material under wet conditions (average annual rainfall: 2,500 mm/a). By 20 ka, they are completely exhausted (Crews et al. 1995). In basaltic parent material, U is mostly contained in the groundmass which dissolves very readily, leaving the soil U budget easily dominated by dust deposition and Fe oxides. Where U is contained in primary minerals that are more resistant to chemical weathering (e.g., biotite and apatite in granitic rocks, illite in sedimentary rocks), the importance of dust deposition and the role of solution-derived secondary phases would be lessened.

The U-series isotope composition of soils developed along a chronosequence has been modeled in a recent study by Keech et al. (2013). The parent material is composed of glacial outwash sediments with deposition ages ranging from 40 ka to 3 Ma. For each soil profile, they averaged the U-series isotope composition of samples collected at different depths and attempted to use the model described in Eq. (1) to reproduce the average activity ratios, knowing the maximum weathering age of each soil profile (i.e., the deposition age). In doing so, they assumed that the known age of the parent material represents an average weathering age for the profile. While it is unclear whether an average activity ratio for a given soil profile has any significance in terms of pedogenic processes, the average weathering age of a soil profile should be a value between 0 and the age of the parent material. The authors used the model described by Eq. (1) but could not reproduce the observed average values for ($^{234}\text{U}/^{238}\text{U}$) and ($^{230}\text{Th}/^{238}\text{U}$), which showed a decrease with increasing age. To explain this discrepancy, the authors proposed a two-stage model where labile U is mobilized first, followed by the mobilization of U in crystal lattices during mineral dissolution. This two-stage model assumes that the parent material was in secular equilibrium prior to soil formation. However, in this case, the parent material is an unconsolidated sediment and is likely to have already undergone significant weathering. This pre-deposition weathering episode would have imparted a disequilibrium to the parent material which would have decayed away only over >300 ka (assuming closed system, which is unlikely during the deposition of an alluvial sediment). Therefore, the greater disequilibrium observed in younger soils may simply be the result of pre-deposition radioactive disequilibria (with ^{234}U and ^{230}Th excesses over ^{238}U) which had not yet decayed away. Thus, there is no need for a two-stage model. Without knowing the U-series isotopic composition of the parent material (which was not sampled), it is not possible to derive reliable time information from this work.

Andersen et al. (2013) have studied the U-series isotopic compositions of soils from a chronosequence formed by glacier retreat in Scotland. The parent material is composed of alluvial sediments deposited in fluvial terraces with ages between 0.1 and 13 ka. At this location, the authors observed that, on average, the ($^{234}\text{U}/^{238}\text{U}$) activity ratio decreased with increasing deposition age, starting with values >1 , similarly to what was observed in Keech et al. (2013), but ($^{230}\text{Th}/^{238}\text{U}$) increased with deposition age, from values initially <1 . The model described in Eq. (1) was used to determine ^{238}U dissolution coefficients for 5.6-ka- and 13-ka-old soils, assuming that the soil weathering age was the same as the deposition age. However, here too the parent material was assumed to be in secular equilibrium. This is unlikely to be the case because soils were developed on fluvial sediments, which were unlikely to be at secular equilibrium at the onset of soil formation (as observed in all fluvial sediments; see the review in Dosseto et al. (2008a)). The decrease in ($^{234}\text{U}/^{238}\text{U}$) with soil age could reflect loss of ^{234}U via recoil or more likely (as pointed out by the authors) via preferential leaching. The initial ($^{230}\text{Th}/^{238}\text{U}$) <1 in the parent material could be explained as the sediment is likely to be derived from organic-rich hillslopes. The presence of organic acids is known to mobilize Th (Porcelli et al. 1997, 2001; Viers et al. 1997; Andersson et al. 1998; Chabaux et al. 2003), and organic-rich soil horizons can exhibit ($^{230}\text{Th}/^{238}\text{U}$) <1 (Dosseto et al. 2008b; Ma et al. 2010; Chabaux et al. 2013; Suresh et al. 2013). The increase in ($^{230}\text{Th}/^{238}\text{U}$) could be explained by the subsequent loss of U during soil development.

While the study of soil chronosequences is an exciting endeavor with a great potential to improve our understanding of soil processes and the use of U-series isotopes, the different aspects of U-series models need to be carefully considered. For instance, initial conditions (i.e., the composition of the parent material) must be adequately assessed in order to apply the appropriate model parameters.

Weathering Rinds

In the early stages of weathering, the parent rock can sometimes develop rinds of weathered material. The measurement of U-series isotopes on a depth profile across the pristine core and the outer weathering rinds can be used to infer how fast the weathering front propagates into the rock. As shown above, it is expected that U is lost preferentially compared to Th and ^{234}U preferentially to ^{238}U , so increasing ($^{230}\text{Th}/^{238}\text{U}$) and decreasing ($^{234}\text{U}/^{238}\text{U}$) activity ratios, respectively, should develop with time. However, in a study of weathering rinds developed on a basaltic clast from a 125-ka-old alluvial terrace in Costa Rica, Pelt et al. (2008) observed the opposite with ($^{230}\text{Th}/^{238}\text{U}$) < 1 and ($^{234}\text{U}/^{238}\text{U}$) > 1 in the most extensively weathered parts of the rinds. This was interpreted as the result of (i) the conservative behavior of Th and (ii) external input of U from soil solutions having ($^{234}\text{U}/^{238}\text{U}$) > 1 , with minimal loss of U during weathering. The input of U was modeled, resulting in a rind formation rate of 0.5 ± 0.2 mm/ka (Table 2). In another study, Ma et al. (2012) also found ($^{230}\text{Th}/^{238}\text{U}$) < 1 and ($^{234}\text{U}/^{238}\text{U}$) > 1 in weathering rinds from a basaltic clast from Guadeloupe Island. They inferred a rind formation rate of 0.18–0.24 mm/ka (Table 2). These rates are three orders of magnitude lower than what has been inferred considering the scale of the weathering-profile development for basaltic lithologies (Dosseto et al. 2012). As explained in Navarre-Sitchler and Brantley (2007), this apparent discrepancy stems from the fractal nature of the weathering advance rate, its value being largely controlled by the length scale over which it is measured. This is a consequence of the variable spatial resolutions used to measure the surface area of the weathering front (from the 10^{-3} m scale when studying weathering rinds to the meter scale when investigating weathering profiles). Navarre-Sitchler and Brantley (2007) showed that it is possible to compare weathering advance rates across length scales by calculating the roughness of the weathering front at each length scale, using the fractal dimension characteristic of the weathering advance rate (for instance, ~ 2.3 for basaltic weathering).

In a weathering profile developed over a granitic corestone in Puerto Rico, Chabaux et al. (2013) also quantified the rate at which weathering-rind formation advances into the corestone and estimated a value of 52 ± 13 mm/ka. Interestingly, this is similar to the saprolite production rate inferred in the same profile (Table 2). This can be explained by the small length scales of weathering-rind development studied by Pelt et al. (2008) and Ma et al. (2012) measured in millimeters, compared to the weathering rinds studied by Chabaux et al. (2013), which cover a length scale similar to that of the weathering profile developed above them.

Implications for Landscape Evolution

A compilation of calculated regolith and soil production rates, similar to the one shown in Dosseto et al. (2012), allows us to make several observations concerning the development of weathering profiles (Fig. 6). Note that these observations need to be considered with caution, given the small number of studies published so far. However, they hint at some aspects of landscape evolution that are worth investigating.

It has been known for a long time that different rocks weather at different rates, depending on the susceptibility to dissolution of the minerals that compose them. This is illustrated on Fig. 6, where in Puerto Rico, regolith production over a volcanoclastic sedimentary rock occurs at a rate more than six times faster than over granodiorite. However, parent material composition does not appear to play a strong role for soil production: soils over a shale are produced at about the same rate as those produced over a granitic rock (Fig. 6). This may imply that soil production is mostly driven by physical weathering, via the mechanical action of plants and animals, rather than by chemical weathering.

The role of climate (runoff, temperature) on regolith production is not clear from results shown in Fig. 6: granitic profiles seem to develop at similar rates across a range of climatic conditions. While it is possible that regolith production rates that are lower than expected in Africa and the Amazon may be the consequence of thick weathering profiles shielding the weathering front from meteoric waters, profiles in Puerto Rico and southeastern Australia have similar thicknesses and production rates despite very different climatic conditions.

Erosion rates in lowlands of western Africa and the Amazon are expected to be <10 mm/ka (Gaillardet et al. 1997; Wittmann et al. 2010). In contrast, Larsen (2012) has estimated long-term hillslope erosion rates in the Rio Icacos basin of Puerto Rico to be ~ 75 mm/ka, mostly driven by landslides. Despite about an order of magnitude difference in erosion rates, regolith production rates for these granitic profiles are relatively similar. They exceed erosion rates in tropical lowlands, while they are similar to or lower than erosion rates in Puerto Rico. This could suggest a decoupling between the surface (where erosion occurs) and the weathering front. The advance rate of the weathering front seems to be most sensitive to the composition of the parent material, showing similar values for granitic profiles across a range of climatic conditions and erosion rates.

Gaps in Knowledge

The models described above are intended to track the U-series isotope composition of minerals derived from the parent rock, whether they are residual primary minerals or secondary minerals formed during incongruent dissolution of primary minerals. Existing studies have focused on bulk material (regolith, soil, sediments). As explained above, the regolith is a complex mixture of primary minerals (derived from the parent rock), secondary minerals precipitated from soil pore water (e.g., carbonates and Fe-Mn oxyhydroxides), allochthonous minerals (via dust deposition), and organic matter (Fig. 3). Each of these phases is likely to have its own U-series isotope composition. Thus, the application of the U-series models is complicated by the contribution of each of these components to the isotopic composition of the bulk sample. Future works should investigate techniques to remove these phases either physically (e.g., mineral separation; (Menozzi and Dosseto 2013; Rihs et al. 2013)) or chemically (e.g., sequential extraction; (Schultz et al. 1998; Blanco et al. 2004; Martin et al. submitted)). Until then, we will still be relying on whichever phases control the U budget of the samples. If the U budget is controlled by only a single primary phase or a secondary phase derived from primary minerals, the models may provide reliable results. If the U budget is controlled by more than one primary phase or secondary phase derived from primary minerals, there might be some noise in the data that make the models less straightforward to apply. If controlled by a mixture of primary and associated secondary minerals, as well as solution-derived secondary minerals, allochthonous minerals, or organic matter, it is likely that the models will yield less than straightforward information. Finally, if the U budget of the samples is controlled by solute-derived secondary minerals, allochthonous minerals, or organic matter, the models will provide meaningless information in terms of weathering age, as defined above. Thus, the future of this technique depends on our ability to understand the U-series contributions from the various components involved and how they impact the overall compositions from which the models are developed.

Conclusions

U-series isotopes in weathering products (weathering rinds, regolith, sediments) allow us to place time constraints on weathering processes. These then can be used to determine the rate of formation of weathering profiles (*regolith production rates*). Results from available studies, when combined

with other tools like cosmogenic isotopes, provide unprecedented insights on the development of weathering profiles and landscape evolution. Results from these studies show that climate seems to have a secondary role on regolith production rates. Instead, the primary control on regolith production appears to be the composition of the parent material. Under tropical climates, for instance, regolith can be produced ~ 6 times faster over a volcanoclastic sedimentary rock than over a granodiorite parent. Conversely, soil production seems to be relatively insensitive to the parent material composition: under temperate climates, soil is produced at the same rates over shale and granodiorite. Finally, regolith production rates are similar for sites that show a range of erosion rates. This suggests a decoupling between the land surface and the weathering front. In this case, the topography of the weathering front would be determined by the lithology, while the surface topography is determined by denudation in response to climatic and tectonic conditions.

Several studies have emphasized the role of dust deposition on weathering profile development and in particular on the uranium budget of the soil. While this is taken into account in existing models of U-series isotopic evolution, further work is needed to improve the robustness of the information derived from these models. In order to achieve this objective, innovative chemical and/or physical protocols for sample preparation are important avenues to explore.

Finally, soil chronosequences represent fascinating natural laboratories to test the application of U-series isotope methods and to further improve the quality of information that U-series models provide. However, these studies need to be carefully undertaken, with a full understanding of the assumptions required by each different model.

With these considerations in mind, it is clear that, combined with other geochronological and geochemical techniques, U-series isotopes supply us with an ability to better understand the evolution of the Earth's surface. As summarized in this entry, more than 10 years of studies on the topic illustrate the unique prospects that this technique offers.

Cross-References

- ▶ [Aquifer Characteristics \(U-Series\)](#)
- ▶ [Cements, Pedogenic \(U-Series\)](#)
- ▶ [Cosmogenic Nuclide Dating](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Paleosol](#)
- ▶ [Radiation and Radioactivity](#)
- ▶ [Radiation Defect](#)
- ▶ [U-Series Dating](#)

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Exhumation (Thermochronology)

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Synonyms

[Denudation](#)

Definition

Exhumation is the vertical upward movement of a rock particle toward the Earth's surface.

Introduction

Exhumation is the vertical upward movement of a rock particle toward the Earth's surface or, more generally, the vertical upward component of a rock-particle path with respect to the Earth's surface. The opposite vertical movement (downward with respect to the Earth's surface) is called burial. Exhumation rate is the vertical upward component of the velocity at which rocks move with respect to the Earth's surface.

Exhumation, Denudation, and Erosion

Usage of the term exhumation with respect to the similar terms erosion and denudation is not rigorously defined. “► [Erosion](#)” is often used to refer to the *physical processes* that remove material from the Earth's surface, whereas denudation and exhumation are commonly used in reference to the movement of rocks with respect to the Earth's surface and are therefore *geometrical quantities*. However, the term erosion is also used in the latter context when referring to relatively short (historical to millennial) timescales. In contrast, exhumation or denudation refers to longer (geological) timescales and/or larger (regional) spatial scales. The distinction between exhumation and denudation is even more subtle: in one usage (Ring et al. [1999](#)), exhumation refers to the upward movement of rocks with respect to a reference frame fixed to the Earth's surface, whereas denudation refers to the downward movement of the Earth's surface with respect to a reference frame fixed to the rock. In another usage (Summerfield and Brown [1998](#)), the term exhumation is reserved for rocks or surfaces that have previously been buried, whereas denudation is the more general term (i.e., a granite can only be denuded, not exhumed, unless it was denuded in a previous cycle and subsequently reburied; a sedimentary rock or erosion surface can be buried and subsequently exhumed). Most workers, however, consider exhumation and denudation to be synonyms and use the two terms interchangeably.

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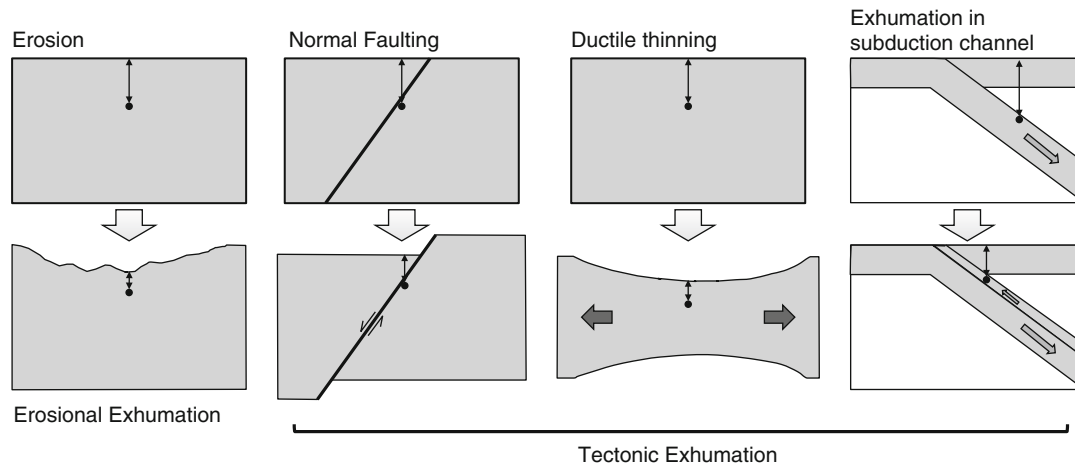


Fig. 1 Schematic depiction illustrating exhumation of rocks by different mechanisms: erosion (erosional exhumation), normal faulting, ductile thinning, exhumation in subduction channel (collectively known as tectonic exhumation). *Top panels* show initial situation, *bottom panels* show situation after exhumation of rock particle (black dot). Double arrows show depth of rock particle below surface before and after exhumation. Shaded regions represent the crust; other arrows indicate tectonic movements

Mechanisms of Exhumation

Exhumation of rocks can be caused by various mechanisms (Fig. 1): (1) erosion, by removing rocks from the Earth's surface, diminishes the vertical distance between the underlying rocks and the surface (erosional exhumation); (2) rocks in the footwalls of normal faults will be exhumed by extensional faulting; (3) a less generally inferred mechanism is ductile stretching of the crust, which will lead to pure-shear extension and thinning, thereby diminishing the vertical distance between the surface and a rock sample; (4) continental rocks that are brought to great depths by subduction can be subsequently buoyantly exhumed in a subduction channel, by replacing denser surrounding mantle rocks. The latter three mechanisms collectively contribute to tectonic exhumation. The most generally inferred exhumation mechanism is erosional exhumation. Tectonic exhumation by normal faulting is an efficient mechanism in metamorphic core complexes, which are exhumed along extensional detachments that can accumulate several tens of kilometers of extension. Buoyant exhumation of deep rocks is limited to subduction settings, while exhumation by ductile stretching of the crust is rarely invoked. The opposite mechanisms will lead to burial of rocks: sedimentary burial beneath an accumulating pile of sediments, tectonic burial in the footwall of a thrust fault, burial by ductile pure-shear shortening and thickening, and deep burial in subduction zones.

Measuring Exhumation

There is no direct way of measuring the amounts or rates of erosional exhumation. The amount of tectonic exhumation by normal faulting or ductile extension and thinning can, in theory, be quantified using structural or tectonic markers such as extensional fault offsets or strain markers. In practice, however, these are rarely sufficiently preserved to allow such reconstruction. If rocks have been buried sufficiently deeply to be metamorphosed, metamorphic pressure-temperature estimates allow quantifying the amount of exhumation; such measures are commonly used to quantify buoyant exhumation of rocks in subduction settings, for instance. The most generally

employed techniques for quantifying the amount and rates of exhumation on geological timescales rely on ► **Thermochronology** data. Different thermochronometers (including (U-Th)/He in apatite, titanite, and zircon; fission tracks in apatite, titanite, and zircon; K-Ar or ^{40}Ar - ^{39}Ar in K-feldspar, mica, and hornblende) are characterized by different closure temperatures (varying from $\sim 70^\circ\text{C}$ for the apatite (U-Th)/He system to $\sim 500^\circ\text{C}$ for the hornblende ^{40}Ar - ^{39}Ar system). Determining the ages of any subset of these different systems in an exhumed rock sample will provide information on whether that sample was buried deeply enough to have experienced sufficiently high temperatures to reset a specific thermochronometric system (allowing a minimum amount of exhumation to be established) and when the sample last cooled through the closure temperature while being exhumed toward the surface (allowing an exhumation rate to be estimated). All of these methods provide a measure of cooling (rate) in a thermal reference frame, however; converting this to an exhumation (rate) in a spatial reference frame requires estimating (or guessing) the geothermal gradient at the time of cooling through the closure temperature. Additional constraints on exhumation rates and pathways can be obtained by combining samples with a known spatial relationship to each other, for instance, by using their age-elevation relationship. Note that exhumation refers to the vertical upward component of motion of a rock particle with respect to the surface. Because both temperature and pressure gradients are (close to) vertical in the Earth's crust, metamorphic pressure-temperature estimates combined with thermochronology yield estimates of exhumation. However, in many orogens, particle paths have large horizontal components as well. Therefore, cumulative amounts of surface erosion may be very much larger than the total amount of exhumation (Batt and Brandon 2002).

On much shorter (millennial) timescales and smaller (metric) spatial scales, in situ produced terrestrial cosmogenic nuclide dating also allows quantification of erosion/denudation rates.

Uplift Versus Exhumation

Confusion remains widespread between the terms and concepts of uplift versus exhumation, even though the difference between these has been made clear more than 20 years ago (England and Molnar 1990). While exhumation refers to the vertical upward movement of rocks with respect to the Earth's surface, uplift refers to vertical upward movement of rocks (rock uplift) or the Earth's surface (surface uplift) with respect to an external reference frame such as sea level (Fig. 2). The above-cited techniques are not able to determine either surface or rock uplift, which require a measure of paleo-elevation with respect to a distinct datum, such as sea level. The three measures are not totally independent, however: by definition, rock uplift is the sum of surface uplift and exhumation.

Summary

Exhumation is the vertical upward movement of a rock particle toward the Earth's surface. Although subtle differences exist in meaning, most workers consider the terms exhumation and denudation as synonyms; both are geometrical quantities representing a diminution of overburden above a rock particle. Different mechanisms can lead to exhumation of rocks; these are classified as erosional exhumation or tectonic exhumation. The most common method to quantify and date exhumation is

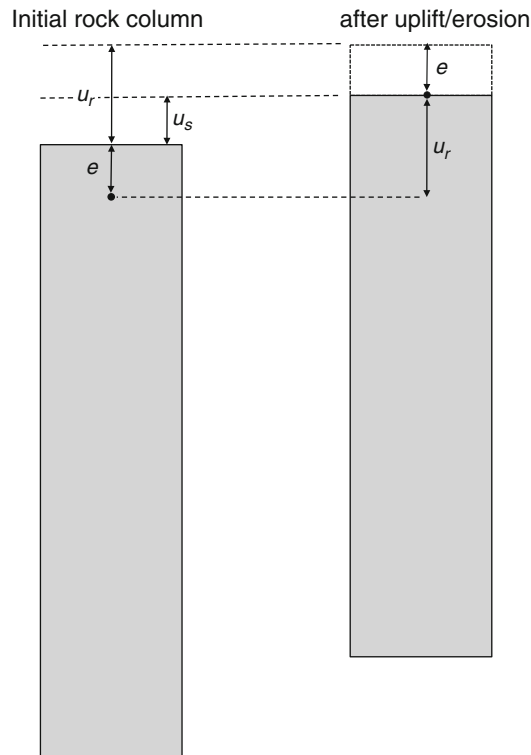


Fig. 2 Schematic depiction showing relationships between rock uplift (u_r), surface uplift (u_s), and erosion/exhumation (e). *Shaded rectangles* represent rock columns; *open rectangle* represents eroded material; *black dot* indicates exhumed rock particle. Note that thermochronological or thermobarometric methods record the amount of exhumation, not (either rock or surface) uplift

by thermochronology; if the exhumed rocks were previously buried sufficiently deeply to be metamorphosed, petrologic pressure-temperature estimates can also be used to quantify the amount of exhumation. Exhumation and uplift are different quantities and no direct measure of (either surface or rock) uplift currently exists.

Cross-References

- [Alpine Terranes \(K-Ar/Ar-Ar\)](#)
- [Apatite](#)
- [Ar-Ar and K-Ar Dating](#)
- [Cosmogenic Nuclide Dating](#)
- [Erosion Rate \(Cosmogenic Nuclide\)](#)
- [Fault Zone \(Thermochronology\)](#)
- [Fission Track Dating](#)
- [Metamorphic Terranes \(K-Ar/Ar-Ar\)](#)
- [Minerals \(Ar-Ar\)](#)
- [Tectonic Processes \(Thermochronology\)](#)
- [Thermochronology, Detrital Zircon](#)
- [Thermochronology, Landform Evolution](#)
- [\(U-Th/He\) Dating](#)

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Fault Zone (Thermochronology)

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Synonyms

⁴⁰Ar-³⁹Ar dating; Ar-Ar dating; Brittle fault dating; Clay gouge; Illite

Introduction and Definition of Brittle Fault Dating

Dating of deformation revolutionized our understanding of crustal evolution by inserting the element of time and rate into strain and regional geology. Middle and deep crustal faults (>10–15 km depth) deform in a temperature regime that promotes growth of various mineral phases containing radiogenic elements, which allow direct and indirect dating of deep fault zones (e.g., van der Pluijm et al. 1994). On the other hand, shallow crustal faulting occurs in the brittle regime, where growth of suitable phases for dating is much more limited. The exception is the K-bearing mineral illite, which is widespread and can be used for dating with K-Ar and Ar-Ar methods in a range of settings, from diagenesis to deformation (Kelley 2002). K-Ar dating has been successful in many areas (e.g., Clauer et al. 1997, 2012; Zwingmann et al. 2010), while others focus on Ar-Ar dating (e.g., Haines and van der Pluijm 2008; Yun et al. 2010). This entry describes the use of Ar-Ar chronology to date brittle faults, including the mineralogic characterization of samples, Ar-Ar systematics and clay dating, and an example application. Application of illite age analysis (IAA) to fault dating has the following benefits: very small sample volumes can be analyzed, potassium and argon are measured simultaneously, and it has high precision. Regardless of the dating approach, separation of grain-size fractions and characterization and quantification of illite are key to reliable ages, requiring the integration of quantitative X-ray analysis.

Illite Characterization and Quantification

Illite-bearing samples of fault rock, herein called clay gouge (Vrolijk and van der Pluijm 1999), are separated into multiple size fractions. Crushed rock is placed in an ultrasonic bath for deflocculation and separated into size fractions using centrifuge settling following Stoke's law. A sample of fault rock is separated into three or four size fractions, in the range of <2.0 to <0.02 μm; samples containing feldspar may require <0.5 μm as the upper size limit to avoid contamination. To characterize bulk mineralogy, oriented clay slurry mounts are analyzed with X-ray diffractometer (XRD) by scanning from 2° to 50° 2Θ (Cu Kα) of both air-dried and glycolated samples (Moore and Reynolds 1997). If carbonate minerals obscure peaks required for quantification of illite polytypes, size fractions of gouges are treated with a weak (~1 N) acetic acid solution after separating material for use in ⁴⁰Ar-³⁹Ar dating. A separate aliquot is used to limit any effects of acid treatment on Ar and K retention.

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To determine the crystallite size and diagenetic grade of gouge, oriented slurry samples of each size fraction are scanned from 2° to $20^\circ 2\Theta$ using an X-ray diffractometer. If appropriate, the percent illite in illite-smectite (%I in I-S) is determined using the method of Środoń (1980) and diffraction patterns are modeled using the program NEWMOD[©] (Reynolds and Reynolds 1996). Illite crystallinity (IC), which reflects the thickness distribution of illite crystallites, is determined by measuring the full width at half maximum (FWHM) of the 001 illite peak in $^\circ 2\Theta$ (Kübler 1968), calibrated by Warr and Rice's (1994) method and standards. Crystallite thickness is calculated using the Scherrer equation (Drits et al. 1997).

Illite age analysis requires quantifying the percentages of the two main polytypes of illite: the higher temperature (detrital) $2M_1$ polytype and the lower temperature (authigenic) $1M/1M_d$ polytype. Standard-oriented X-ray mounts tend to obscure peaks that have non-(00l) indices, so randomized powder mounts are made using an end-packer device (after Moore and Reynolds 1997). Illite polytypes are quantified by matching natural XRD patterns with synthetic XRD patterns created using WILDFIRE[©] software (Reynolds 1993). The program allows different properties for $2M_1$ and $1M/1M_d$ illite and varying parameters such as randomness, crystallite size, hydration state, percentage cis- and trans-vacant interlayers, and smectite interlayers. We use a spreadsheet program to match measured XRD patterns to the synthetic XRD patterns, as illustrated in Fig. 1. Typical precision for illite polytype quantification is 2–3 %.

^{40}Ar - ^{39}Ar Chronology of Clays

The K-Ar dating technique is based upon the assumption that radiogenic ^{40}Ar (i.e., $^{40}\text{Ar}^*$) produced by the beta-decay of ^{40}K is quantitatively retained within a mineral structure. Given this assumption, the $^{40}\text{Ar}^*/^{40}\text{K}$ ratio is effectively a measure of the time since a mineral became closed to Ar loss. The ^{40}Ar - ^{39}Ar technique extends the K-Ar method by using the fast neutron reaction $^{39}\text{K}(\text{n,p})^{39}\text{Ar}$ to produce ^{39}Ar , which is a proxy for ^{40}K , and therefore, the $^{40}\text{Ar}^*/^{39}\text{Ar}$ ratio is used as a measure of the age of mineral. However, unlike the decay reaction that produces $^{40}\text{Ar}^*$, the reaction that forms ^{39}Ar is highly energetic and it causes the resulting nucleus to recoil an average distance of 162 nm within silicate minerals (Turner and Cadogan 1974; Onstott et al. 1995). For most minerals that are dated using the ^{40}Ar - ^{39}Ar method, this recoil distance is considered to be insignificant relative to the average grain size, but in the case of fine-grained clay particles, the average thickness of a grain might be much less than the average recoil distance. This means that ^{39}Ar recoil effects can dominate argon systematics for clay-sized particles, and an approach for collecting any ^{39}Ar lost due to recoil is needed in order to use the ^{40}Ar - ^{39}Ar technique to date clays.

Seidemann (1976) first described a vacuum encapsulation technique, where a sample is placed within an evacuated fused silica capsule. After neutron irradiation, the capsule was cracked open within a vacuum system and the released argon isotopes were analyzed using an attached noble gas mass spectrometer. Subsequently, the technique has been used in several laboratories (e.g., Hess and Lippolt 1986; Foland et al. 1992; Smith et al. 1993), but the most extensive use of the method has been at the University of Michigan.

Smith et al (1993) noted that the quantity of ^{39}Ar released during neutron irradiation, called the recoil gas fraction, was less than anticipated purely from geometrical considerations due to the sample grain size. They attributed the difference to efficient reimplantation of ^{39}Ar between neighboring grains and postulated that the dominant control on the retention of ^{39}Ar during neutron irradiation was the depth of penetration of the recoiled nucleus. In effect, ^{39}Ar retention depends on where the recoiled nucleus stops and does not depend strongly upon grain size or the recoiled

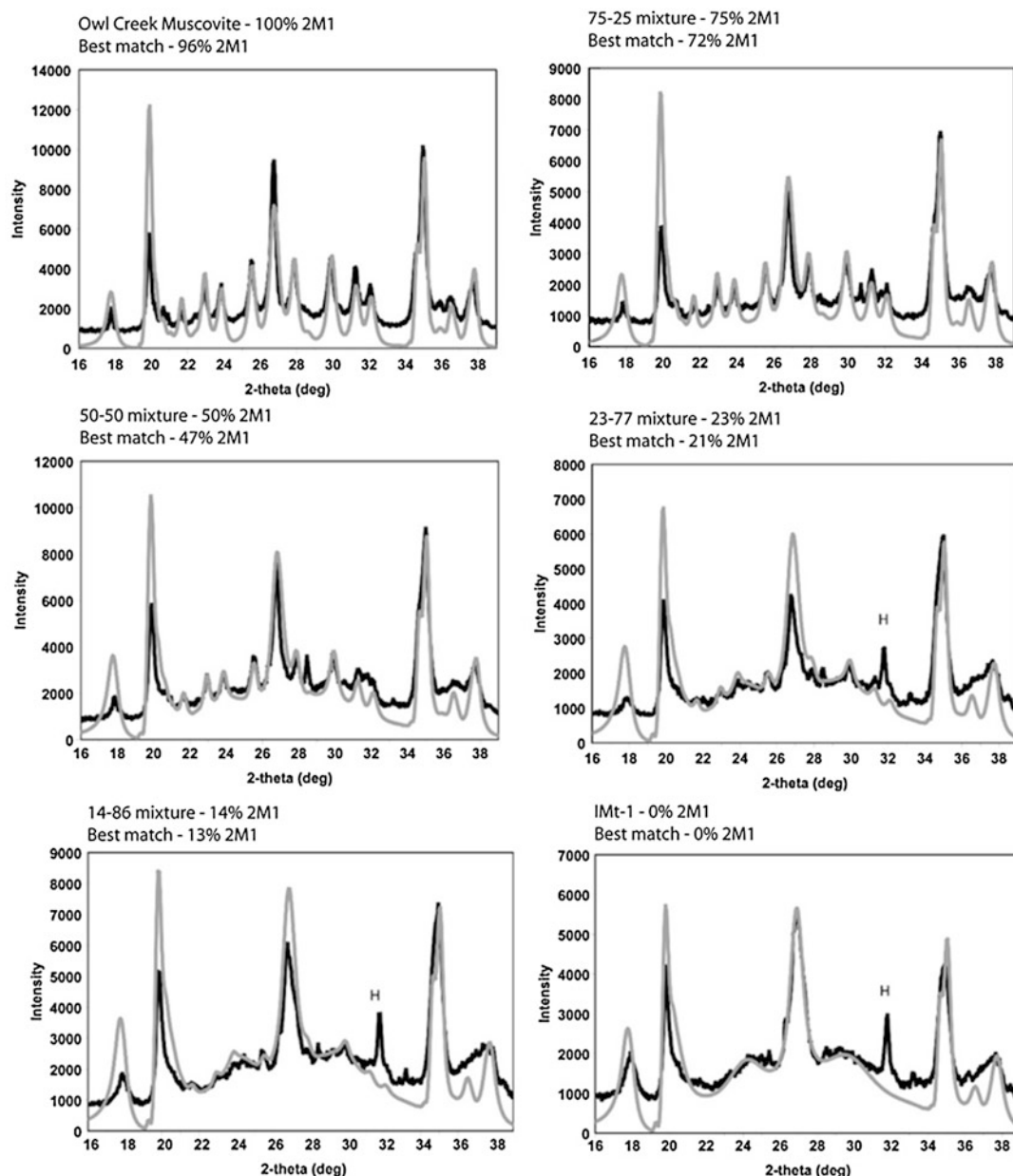


Fig. 1 XRD patterns (*black curve*) for six mixtures of Owl Creek muscovite ($2M_1$) and IMt-1 illite ($1M_d$) and the best-matched models (*gray lines*). Note that for $2M_1$ -rich mixtures, the best matches are obtained from $2M_1$ -specific peaks, while for $1M_d$ -rich mixtures, the best matches fit the entire pattern between 21° and 36° 2θ (From Haines and van der Pluijm 2008)

distance. This point was further supported by the observation that the retained fraction of ^{37}Ar was virtually identical to that for ^{39}Ar despite ^{37}Ar having over twice the expected recoil distance compared to ^{39}Ar (Onstott et al. 1995). Dong et al. (1995) confirmed these observations and observed that the fraction of ^{39}Ar released due to recoil from illite was correlated with the crystallinity index as derived from XRD analysis, with well-crystallized illite having extremely low loss of ^{39}Ar , regardless of grain size. This suggested that the amount of Ar loss due to recoil depends mostly on the nm-scale structural state of illite.

Total Gas Ages and Retention Ages of Illite

Dong et al. (1995) postulated that the retention of ^{39}Ar is controlled by the density of dislocations, defects, and exposed mica surfaces within illite crystal packets. It has long been suggested that Ar can only diffuse along the interlayer regions between the structurally strong 2:1 unit sheets that comprise micaceous minerals (e.g., Hames and Bowring 1994; Kramar et al. 2003). Therefore, it is likely that an Ar atom that arrives within a bounded interlayer will be retained. Given an average illite packet thickness of n 2:1 structural units, there are a total of $2n$ surfaces on these n sheets. Two adjacent 2:1 structural units comprise an interlayer region, and there should be $2n - 2$ internal surfaces and 2 exposed surfaces. Dong et al. (1995) suggested that in this case, the fraction of non-retentive sites is $2/2n = 1/n$.

The ages calculated from both the ^{39}Ar ejected due to recoil and the Ar retained within the sample in the Dong et al. (1995) study (called **total gas ages**) were often too young when compared with other geological constraints. Specifically, well-crystallized epizonal-grade illite was found to give much older ages than lower-grade diagenetic illite within the same sedimentary basin, indicating that the lower-grade, poorly crystallized illite had already lost a significant fraction of its radiogenic ^{40}Ar . Dong et al. (1995, 1997) found that ages calculated without the recoil gas fraction, meaning ages calculated only from Ar that was retained within the sample, gave geologically reasonable values; these were called **retention ages**. This was further confirmed for hydrothermally produced clay minerals by Hall et al. (1997, 2000). These retention ages assume that there is K within both retained interlayer sites as well as in exposed sites in defects, dislocations, and exposed surfaces. K residing in these non-retentive sites will contribute to the total ^{39}Ar inventory; however, any ^{40}Ar produced at these sites will not have been retained over geological time. In effect, the Ar retention ages correct for the loss of radiogenic ^{40}Ar by ignoring any Ar from non-retentive sites.

Subsequently, Dong et al. (2000) found that total gas ages gave stratigraphically correct ages for smectite-rich illite-smectite (I/S), and van der Pluijm et al. (2001, 2006) found that the total gas age model yielded reliable ages for authigenic I/S formed during shallow fault motion. This indicates that in weakly crystallized I/S, defect sites are almost entirely composed of K-poor smectitic layers. Thus, total gas ages and retention ages represent end-member models that are linked to the crystal structure of illite, with total gas ages assuming there is no K in non-retentive sites and with retention ages assuming that non-retentive sites have K concentrations equal to that in internal, retentive interlayer sites.

Illite Age Analysis: Example

The Sierra Mazatán fault is part of a Cordilleran metamorphic core complex in Sonora, Mexico, that separates mid-crustal Paleocene granites and minor gneisses in the footwall from Cretaceous metavolcanics and unmetamorphosed Tertiary sedimentary rocks in the hanging wall (Wong and Gans 2003). XRD pattern matching of size fractions from the fault shows that gouge compositions range from 84 % to 18 % 2M_1 illite and that compositions are positively correlated with grain-size fraction (Haines and van der Pluijm 2008). The corresponding Ar degassing spectra and total gas and retention ages for four samples of coarse to very fine material are shown in Fig. 2.

The retention ages vary nonsystematically, from 19.6 to 20.2 Ma, while the total gas ages are younger and vary systematically with decreasing grain size (18.0–15.5 Ma). Illite crystallinity measurements, recording a small average illite crystallite size, indicate that total gas ages should be used for the dating of these samples, which result in systematically younger ages as the

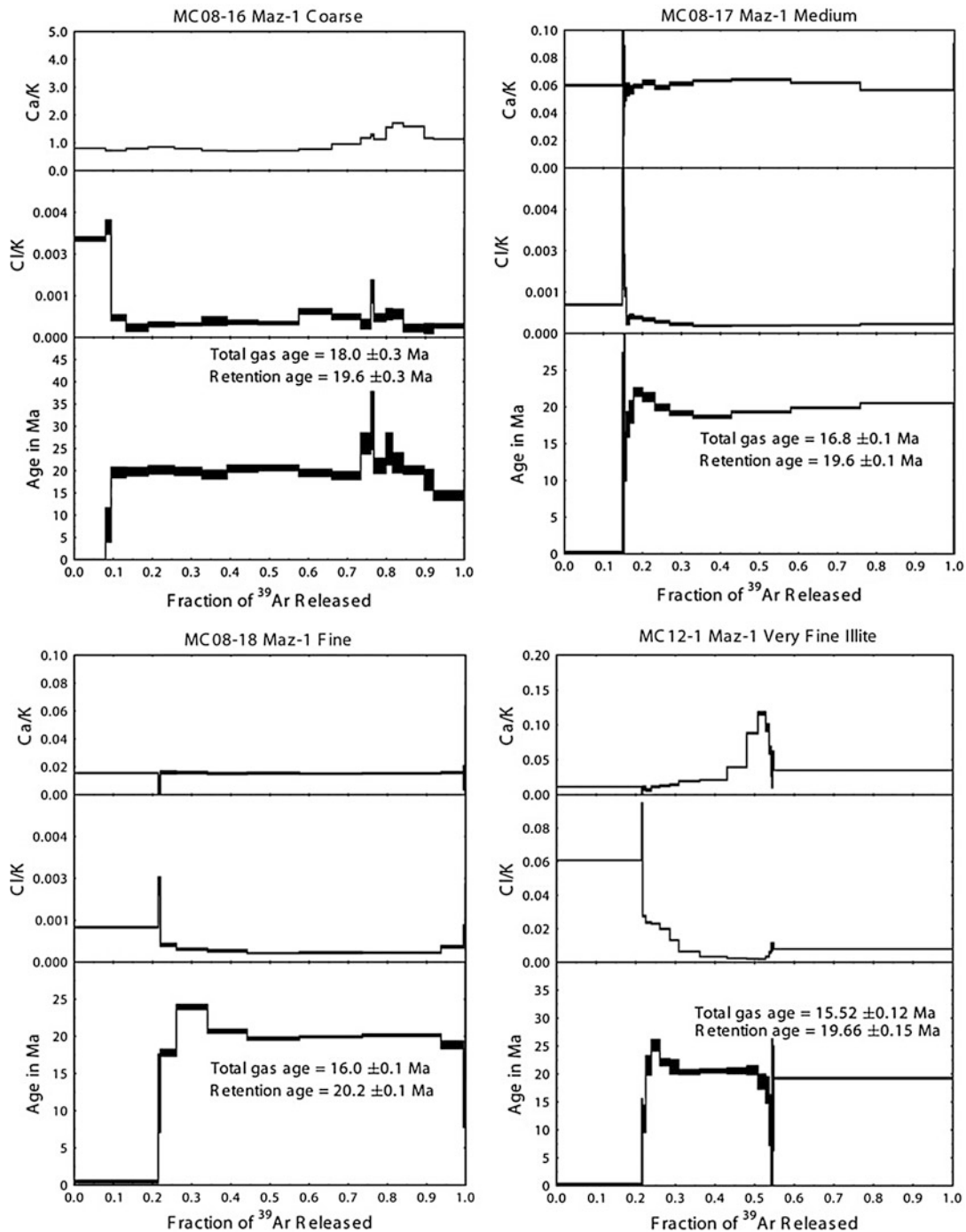


Fig. 2 Ar degassing spectra for four size fractions of the Mazatán fault, showing total gas ages and retention ages for each, as well as Ca/K and Cl/K ratios (Modified from Haines and van der Pluijm 2008)

percentage of detrital 2M_1 illite decreases and authigenic $1\text{M}/1\text{M}_d$ illite increases in finer-grained samples. Plotting age versus % 2M_1 illite for each size fraction and using York regression (Mahon 1996) produces a lower intercept, representing 100 % authigenic illite, of 14.8 ± 0.2 Ma and an upper intercept, representing 100 % mica in the granitic footwall, of 18.7 ± 0.7 Ma (Fig. 3). The extrapolated authigenic illite age supports well-known field constraints on faulting and the upper intercept age matches feldspar cooling ages from these samples (Wong and Gans 2003). The use of

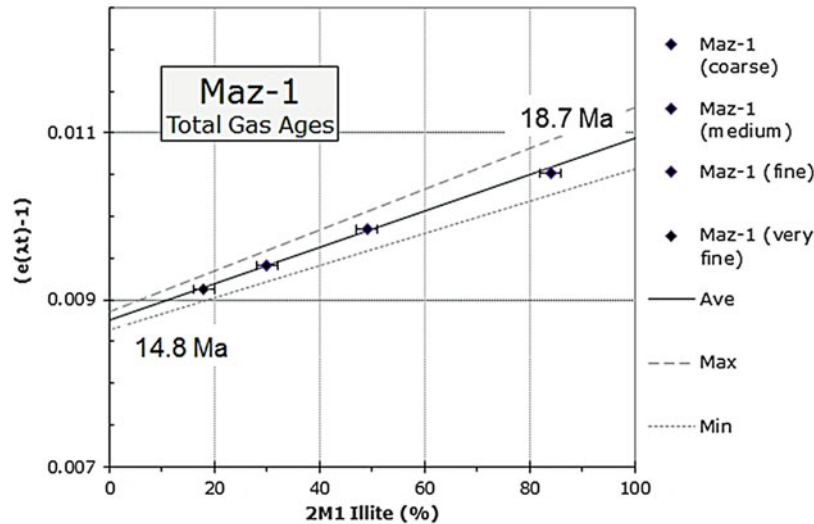


Fig. 3 Illite age analysis plot for gouge from the Sierra Mazatán detachment. Numbers in *bold* are the extrapolated ages for the authigenic (14.8 Ma) and host illite population (18.7 Ma) mixed in the gouge. Percentage host rock illite ($2M_1$) is plotted against the function $(e^{\lambda t} - 1)$ because it is proportional to $^{40}\text{Ar}^* - ^{40}\text{K}$, which in turn is a linear function of the proportion of authigenic and detrital grains. λ is the total decay constant for ^{40}K and t is the apparent age (Reprocessed data from Haines and van der Pluijm 2008)

four size fractions significantly improves the statistics of the age determination over using the minimum of three size fractions, with an age error that is mostly defined by the error in clay quantification and not Ar ages of each size fraction.

Summary and Progress

Illite age analysis combines quantitative X-ray analysis of clay separates with encapsulated sample ^{40}Ar - ^{39}Ar dating. Both illite in illite-smectite (I in I/S) and illite polytype methods offer robust, internally consistent approaches to dating of upper crustal deformation structures that involve the (trans)formation of illitic phases, which is common in natural rocks. It has been reliably applied to shallow faults in multiple regional settings that include reverse, normal, and strike-slip systems and was recently extended to include the dating of fold systems (Fitz-Diaz and van der Pluijm 2013).

Cross-References

- Ar-Ar and K-Ar Dating
- Clays and Glauconites (K-Ar/Ar-Ar)
- Igneous Rocks (K-Ar)
- Mass Spectrometry
- Metamorphic Terranes (K-Ar/Ar-Ar)
- Minerals (Ar-Ar)
- Noble Gas Mass Spectrometer
- Structural Fabrics (K-Ar/Ar-Ar)
- Tectonic Processes (Thermochronology)

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Faults (U-Series)

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Synonyms

[Dating coseismic calcite](#); [Dating fault-related precipitate](#); [Paleoseismicity](#); [U–Th geochronology of syn-tectonic calcite](#)

Definition

The use of U-series geochronology applied to fault-related calcite for dating brittle fault activity.

Introduction

Absolute time constraints on fault activity are an essential part of many plate tectonic and paleoseismic studies, and their potential interpretation in terms of fault seismicity and seismic hazards is well recognized (e.g., Grant et al. 1999; Hee-Kwon and Schwarcz 1995). The introduction of paleoseismological exploratory trenching studies offered the opportunity to determine the number and timing of large paleo-earthquakes and their estimated magnitude and recurrence intervals (e.g., Clark et al. 1972; Sieh 1984). Other studies provided important paleoseismic records recovered in laminated sediments (Ken-Tor et al. 2001; Marco et al. 1996) and damaged speleothems (Kagan et al. 2005; Plan et al. 2010). However, most paleoseismological studies use indirect methods for dating fault movement based on the geochronology of material collected from the displaced or damaged stratigraphic section and not from the fault zone itself. In addition, most paleoseismological dating studies are based on ^{14}C and optically stimulated luminescence (OSL) dating methods, which are both limited to relatively young events [≤ 50 ka for ^{14}C (Ramsey et al. 2012) and ≤ 100 ka for OSL (Huntley et al. 1985)]. U-series dating of fault-related calcite precipitates is therefore an important source of information of both processes occurring in the fault zone during seismic events and of paleoseismic events occurring further back in the geological history.

The use of U-series method for dating fault activity implies temporal association among faulting, fluid circulation, and precipitation processes in the fault zone. For example, calcite dissolution and reprecipitation are common processes in fault zones within host-rock carbonates due to enhanced fluid infiltration processes in the fractured damage zone. In this setting, the formation of secondary calcite may occur during (syn-tectonic), or following (post-tectonic), a faulting event. While U-series ages of syn-tectonic calcite provide constraint on the timing of seismically active period, ages of post-tectonic calcite can be used to constrain the timing of inter-seismic period and/or provide a minimal age for the timing of the deformation event. Identifying syn-tectonic from post-tectonic precipitates therefore represents a fundamental step toward accurate interpretation of the

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U-series age results. Making these interpretations requires a combination of structural, isotopic-geochemical, and geochronological approaches.

Fault-Related Calcite Precipitates in Brittle Fault Zones

Fault-related structures are formed during brittle deformation events and are commonly used as kinematic indicators for strain orientation (Boullier et al. 2004; De Paola et al. 2008) and sense of displacement (Petit 1987). Tension gashes, fault breccias, dilation veins, striation marks, and injection veins are examples for fault-related structures that are potential sites for calcite precipitation (Fig. 1). Calcite precipitated in these fault-related features is a good candidate for the implementation of U-series geochronology for dating fault activity; however, further microstructural and

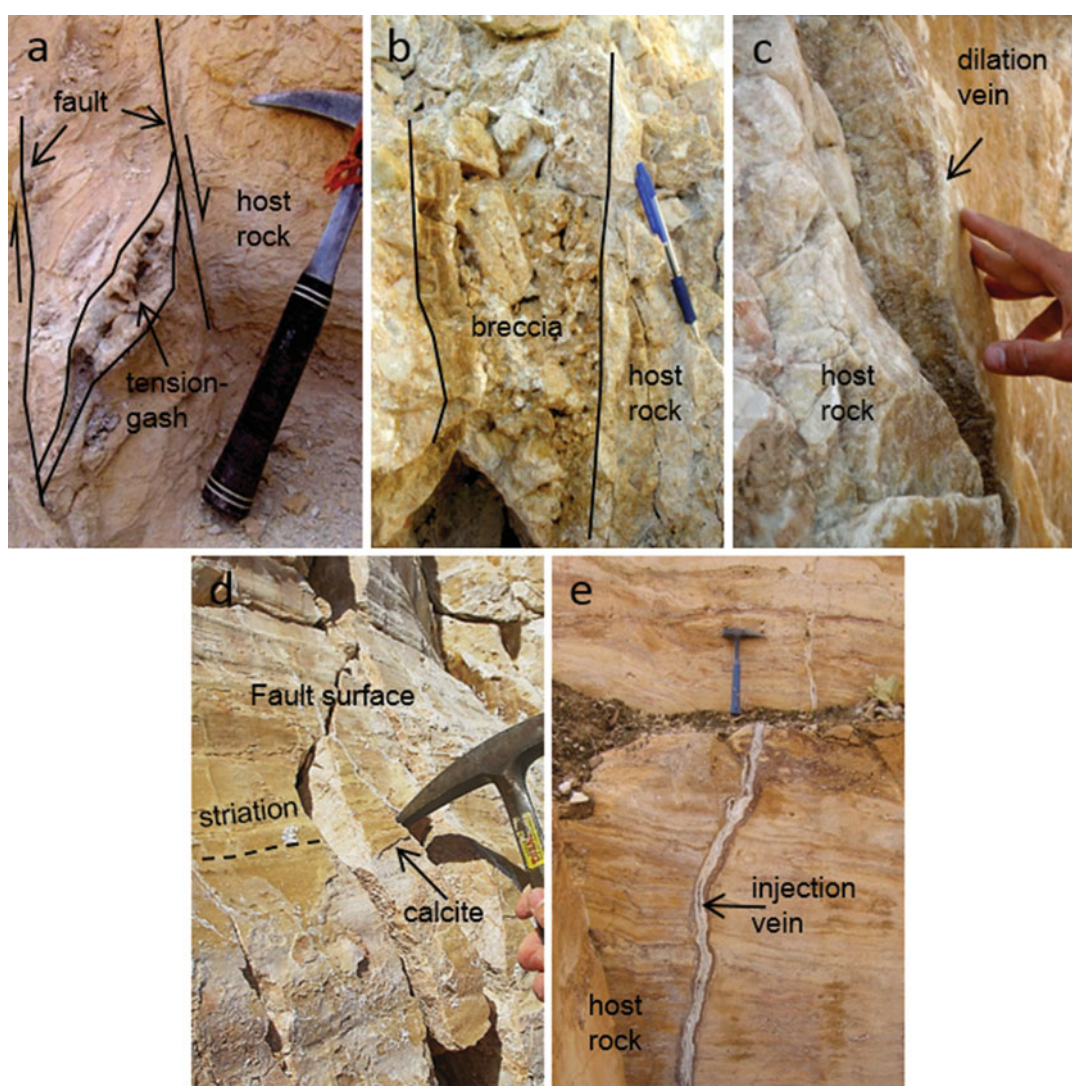


Fig. 1 Fault-related calcite precipitates. (a) Tension gash filled with calcite from the Dead Sea fault zone (DSFZ), Southern Israel (Nuriel et al. 2011); (b) calcite-cemented breccia; (c) calcite-filled dilation vein from the DSFZ, Northern Israel (Nuriel et al. 2012a); (d) calcite coating striation marks from the DSFZ, Northern Israel (Nuriel et al. 2012b); and (e) calcite injection vein from the Pamukkale geothermal fields (Uysal et al. 2009). All fault-related calcite are secondary phases within limestone host rock

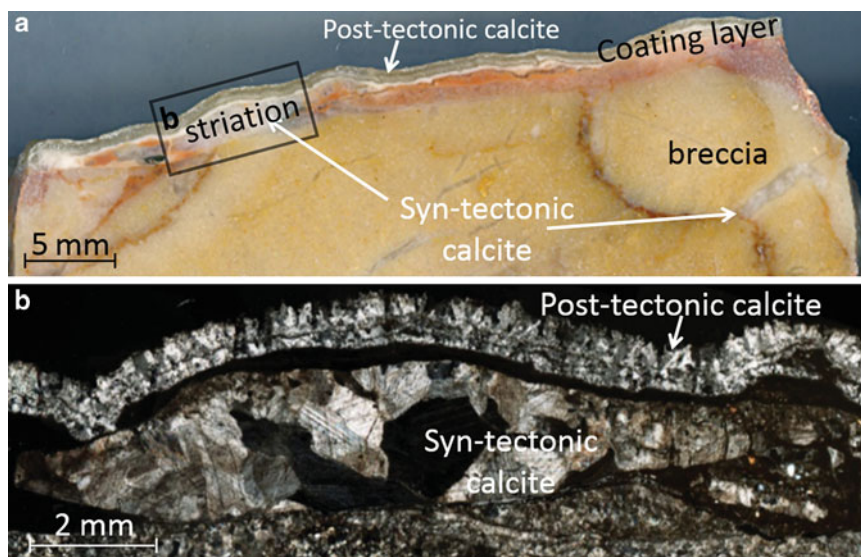


Fig. 2 Microstructures of fault-related calcite. **(a)** Polished slab of a hand specimen taken perpendicular to fault plane and grooves showing the occurrences of syn-tectonic calcite (within striation and breccia) and post-tectonic calcite (coating layer), **(b)** close-up of calcite striation (location is shown in **a**) showing characteristic morphology of syn-tectonic calcite (calcite twins with euhedral crystals and radial growth texture) and post-tectonic calcite (crack-seal texture). Sample is from the DSFZ, Northern Israel (Nuriel et al. 2012b)

isotopic-geochemical characterization is needed in order to determine the temporal association between calcite precipitation and faulting (e.g., syn- or post-tectonic).

Microstructures of Fault-Related Calcite Precipitates

Microstructural studies of fault-related precipitates provide important information on the progressive development of a structure, on temporal changes in precipitation conditions and on growth mechanisms. In particular, the size of displacement along fault asperities will result in the occurrence of either syn-tectonic or post-tectonic precipitates (Gratier and Gamond 1990). Large displacement is associated with a cataclastic-seismic event and the formation of large cavities (several mm in size). These open cavities can be filled with syn-tectonic calcite, characterized with morphologies including twining, euhedral crystals, and radial growth texture (Fig. 2a, b). In contrast, small displacement is associated with aseismic slip, involving dissolution and sealing of successive microcracks (μm in size) by crack-seal mechanism (Ramsay 1980). Calcite that precipitated by crack-seal mechanism should be considered as post-tectonic (Gratier and Gamond 1990) and is characterized with fibrous crystals (Fig. 2b) and surface-parallel arrays of detached overgrowths containing fluid inclusions (Cox and Etheridge 1983; Uysal et al. 2011).

Geochemistry of Fault-Related Calcite Precipitates

The geochemistry of fault-related calcite precipitates can provide important information on the fluids that are responsible for their formation (e.g., Pili et al. 2002). The type and source of fluids and their transport mechanism and residence time in the system can also help determine the time relation between faulting, precipitation, and fluid circulation. Common analytes used to determine fluid

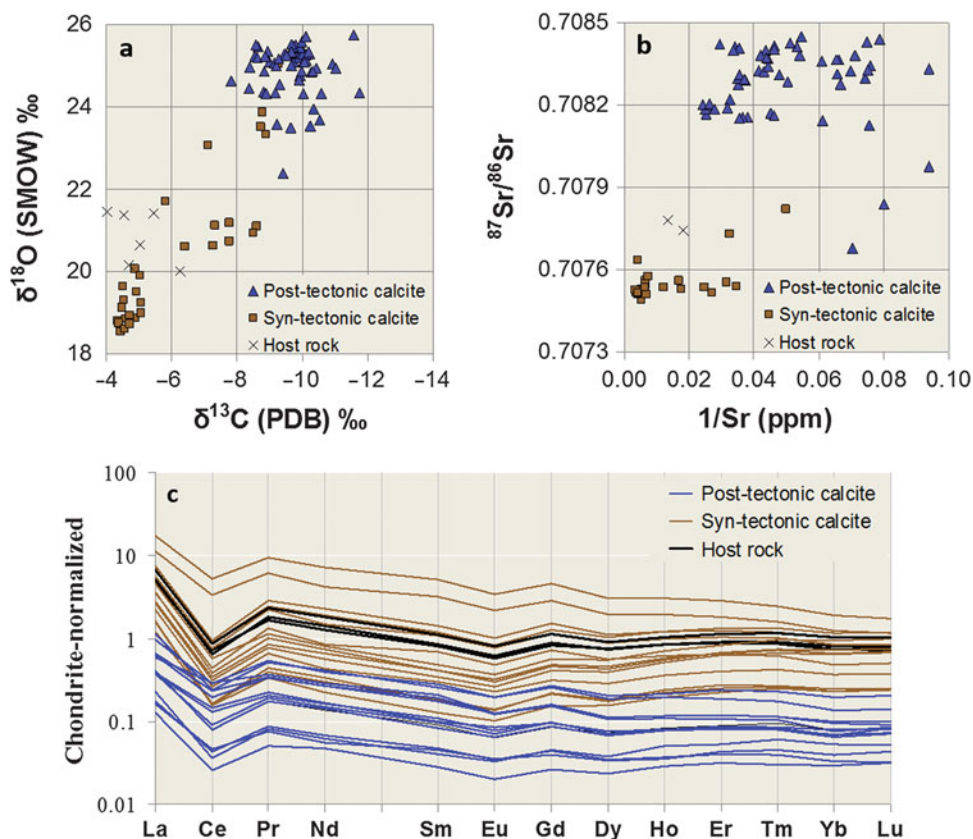


Fig. 3 Geochemistry of fault-related calcite precipitates and host-rock samples from the Dead Sea fault zone (DSFZ), Northern Israel (Modified after Nuriel et al. 2012b). (a) $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ with values given in per mil (‰) relative to Vienna Pee Dee Belemnite (V-PDB) carbonate standard and Vienna Standard Mean Ocean Water (V-SMOW) standard, (b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ concentration (ppm) plot, and (c) chondrite-normalized REE patterns of the different types of calcite precipitates relative to their host rock. Calcite types are marked with different symbols (Chondrite values from Haskin et al. (1971))

source and transportation mechanisms include stable isotopes ($\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$; Fig. 3a), strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$; Fig. 3b), and rare earth element (REE) concentrations (Fig. 3c). Based on these and other parameters, various fluid sources and transportation mechanisms have been proposed for the formation of fault-related calcite precipitates in different tectonic settings, including: (1) earthquake-mobilized fluids (Uysal et al. 2007; 2011), (2) pressurized solutions (Gratier et al. 2002; Nuriel et al. 2012b), (3) meteoric water interacting with host-rock carbonates to various degrees (Labaume et al. 2004; Nuriel et al. 2011; 2012a; Verhaert et al. 2004; 2003), and (4) a mixing of several sources (Boles and Grivetti 2000; Verhaert et al. 2009). In addition, the geochemical-isotopic signature of syn-tectonic and post-tectonic calcite precipitates from the same site (or same sample) can be very different and can reflect differences in the formation mechanisms (see example in Fig. 3).

U-Series Dating of Fault-Related Calcite Precipitates

The U-series dating technique is based on the fact that the ^{238}U decay chain has two intermediate radiogenic and radioactive daughters (^{234}U and ^{230}Th). Both have geologically short half-lives ($\sim 10^5$ years), meaning that the method is appropriate only for dating processes that occurred in the

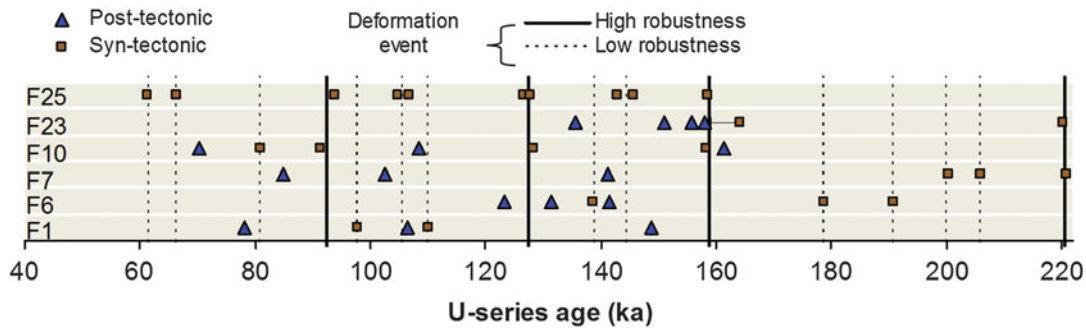


Fig. 4 U-series ages of fault-related calcite from the Dead Sea fault zone, Northern Israel (modified after Nuriel et al. 2012b). U-series ages, in ka, are shown for syn-tectonic (*squares*) and post-tectonic (*triangles*) calcite from different samples (sample names are denoted at the left-side axes). *Solid vertical lines* indicate well-defined (high-robustness) deformation events characterized by coeval development of syn-tectonic precipitates. Post-tectonic calcite is interpreted to form following deformation events during inter-seismic periods. *Dashed vertical lines* indicate moderately defined (low-robustness) deformation events based on single-sample age. Symbols are larger than 2σ age errors

last ~500,000 years (Edwards et al. 1987). Basic assumptions that apply to the U-series dating method include two main points (e.g., Ivanovich and Harmon 1992; van Calsteren and Thomas 2006): (1) daughter nuclides (i.e., ^{230}Th) were not present in the sample at the time of precipitation, and (2) the sample must be a closed system to post-formation migration or addition of any of the radionuclides (i.e., ^{234}U , ^{230}Th). Thus, changes in U/Th isotopic abundance in the system occur only by radioactive decay and growth processes. The first assumption can be validated by the presence of ^{232}Th (Kaufman and Broecker 1965; Ku and Liang 1983), the more common of the two Th isotopes that behaves like a stable isotope due to its long half-life. According to the Kaufman-Broecker concept, if measured $^{230}\text{Th}/^{232}\text{Th}$ activity ratios are low (<20), it is likely that non-authigenic ^{230}Th is also present (i.e., initial ^{230}Th present at the time the calcite was formed rather than forming subsequently by in situ decay of ^{234}U or ^{238}U), and a correction procedure is needed. However, if $^{230}\text{Th}/^{232}\text{Th}$ activity ratios are high (>20), the correction for initial ^{230}Th is negligible. The second assumption is, however, much harder to validate, particularly in syn-tectonic calcite. Unlike dating of corals and speleothems, which commonly exhibit measured activity ratios ($^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$) predicted by U-series isotope evolution in material formed by progressive deposition (continuous growth, see Ku 1965), syn-tectonic precipitates form episodically during different precipitation events and may result in complex patterns of physical growth. As such, it can be much more difficult to evaluate whether U-series isotopes remained closed to secondary mobility. One way to help evaluate resulting ages is to assume closed system behavior and compare ages calculated for syn-tectonic and associated post-tectonic precipitates, which formed continuously during the inter-seismic period from the same site and preferably from the same sample. Dating post-tectonic and syn-tectonic precipitates from the same site may also provide a more complete history for fault activity that includes both the active (seismic) and inactive (inter-seismic) periods. An example for such a record from the Dead Sea fault zone in Northern Israel is shown in Fig. 4.

Conclusion

Microstructural, geochemical, and isotopic signatures of syn-tectonic and post-tectonic calcite precipitated in brittle fault zones reflect different formation mechanisms and temporal relations to faulting events. Therefore, assessment of these features is important for making accurate

interpretations of U-series ages of fault-related calcite. Resulting ages have been used to directly determine the timing of faulting events in many recent studies (Boles et al. 2004; Flotté et al. 2001; Nuriel et al. 2009, 2011, 2012a, b; Uysal et al. 2007; Verhaert et al. 2003, 2004). In addition, U-series ages of both syn-tectonic and post-tectonic calcite precipitates from the same site can shed light on seismic and inter-seismic fault activity.

Cross-References

- ▶ Carbonates, Lacustrine (U-Series)
- ▶ Cements, Pedogenic (U-Series)
- ▶ Fault Zone (Thermochronology)
- ▶ U-Series Dating

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Rubidium–Strontium Dating, Hydrothermal Events

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Definition

Dating hydrothermal events related to the formation of ore deposits by the Rb–Sr dating method

Historical Background

Dating of a hydrothermal event related to ore formation was conducted initially by dating the granite that was regarded as the heat source for the hydrothermal activity and assuming that ore deposition occurred contemporaneously with emplacement of the granite. Indirect dating of alteration minerals such as sericite using K–Ar, Ar–Ar, and Rb–Sr methods was also attempted. Results from these studies, however, have been problematic because of (1) complex associations between ore and alteration minerals and (2) possible multiple hydrothermal events, which can reset chronological information. Gangue minerals can be used as more direct targets of dating. Shepherd and Darbyshire (1981) obtained the Rb–Sr age of 392 ± 5 Myr from fluid inclusions in quartz from the Carrock Fell tungsten vein deposits, northern England. However, the cause of the large variable Rb–Sr ratios observed in their fluid inclusion samples remains uncertain, which suggests mixing of different stages of ore-forming fluids. These problems strongly demand direct dating of ore minerals.

Rb–Sr Dating of Sphalerite from Mississippi Valley-Type Ore Deposit

Most long-lived radioactive nuclides, aside from Re, do not enter into metal sulfides, which makes direct dating of ore deposits difficult. Sphalerite from Mississippi Valley-type (MVT) ore deposits was the first example of successful dating of a sulfide mineral by Rb–Sr method. Mississippi Valley-type deposits are carbonate-hosted lead–zinc deposits. These deposits are regarded as the product of large-scale fluid movements in the upper crust. However, they are formed from warm basinal brines and are not hydrothermal deposits in the strict sense. Direct dating of an ore mineral, sphalerite, was attempted by Nakai et al. (1990) and Nakai et al. (1993). In those analyses, sphalerite samples were crushed and leached in purified water to separate fluid inclusions, which represent solutions trapped at the time of ore-mineral formation. Sphalerite solid residues contain Rb and Sr of 0.05–0.5 and 0.3–2 ppm, respectively, with variable $^{87}\text{Rb}/^{86}\text{Sr}$ of 0.2–2. Water from fluid inclusions trapped in these same grains, however, contains high Sr with low and limited $^{87}\text{Rb}/^{86}\text{Sr}$ of 0.05–0.26. Figure 1 shows a Rb–Sr isochron plot of sphalerite residues and their fluid inclusions from Coy Mine, Mascot–Jefferson City district, eastern Tennessee, United States. The Rb–Sr isochron of sphalerite solid residues yields an age of 377 ± 29 Ma. The isochron was regressed on data for solid residues without using fluid inclusion data. The point for C15, which was more deformed than the other samples, was not considered in the age calculation. The resulting age ruled out any genetic

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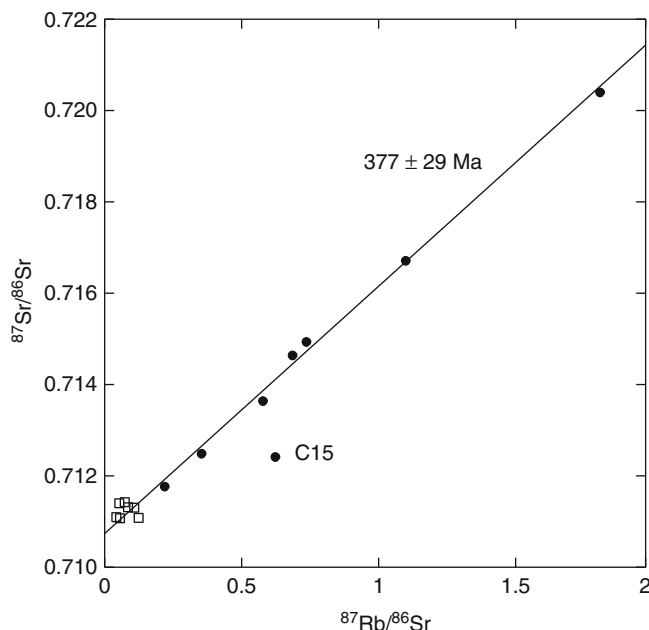


Fig. 1 Rb–Sr isochron of sphalerites from Coy Mine, Mascot–Jefferson City district, east Tennessee (Data were taken from Nakai et al. (1990)). Data for sphalerite residues are shown as *filled circles*, whereas data for fluid inclusions are shown as *open squares*. The isochron was fitted to data for sphalerite residues analyzed after removing solutions contained in fluid inclusions, excluding data from C15 (see text)

connection between mineralization and the Alleghenian orogeny (330–250 Ma). Combining the Rb–Sr age of sphalerites from the Immel Mine, it was concluded that MVT deposits in the eastern United States were formed by brine migration triggered by the earlier Acadian orogeny (380–350 Ma). Sphalerites from Pine Point district, Canada (Nakai et al. 1993); from the West Hayden ore body, Wisconsin, in the Upper Mississippi Valley district (Brannon et al. 1992); from the Polaris Mine in the Canadian Arctic Archipelago (Christensen et al. 1995a); and from Blendevalle, Western Australia (Christensen et al. 1995b), were dated using this method.

Nakai et al. (1993) reported that sphalerites from Daniel’s Harbour Mine, Newfoundland, Canada, and from Monte Cristo Mine, Arkansas, United States, showed no isochron. The samples used for dating might be mixtures of sphalerites from different stages of ore deposition. Nakai et al. (1993) reported that minute amounts of inherited silicate inclusions might have disturbed the Rb–Sr isotopic system in sphalerites from the Monte Cristo Mine because the samples contained very low Sr.

Validity of Rb–Sr Isochron Age

The observed variable Rb–Sr ratios in sphalerite residues engender some doubt about whether the Rb–Sr correlations were formed by mixing of sphalerite and (1) a high Rb–Sr phase, such as a silicate mineral, or (2) a low Rb–Sr phase, such as a fluid inclusion.

Nakai et al. (1993) analyzed Rb and Sr isotopes in K-feldspars from unmineralized carbonate rocks in the Immel Mine. Their results showed that K-feldspar data plotted above an isochron formed by sphalerite. They concluded that mixing between K-feldspar and other components with low Rb–Sr ratio could not have formed the observed sphalerite isochron.

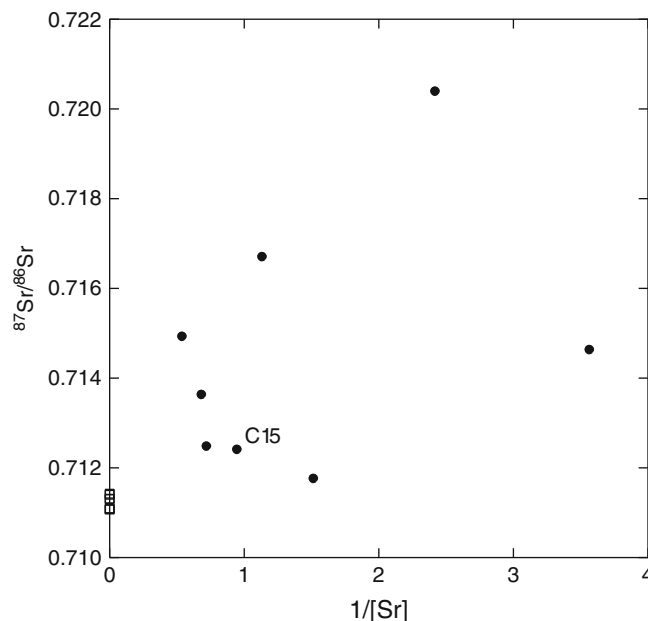


Fig. 2 Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus reciprocal Sr concentration ($1/[\text{Sr}]$) for sphalerites from Coy Mine, Tennessee (Data are from Nakai et al. (1990)). Symbols are the same as those in Fig. 1. Sphalerite residues do not form a *straight line*, ruling out the possibility that Rb–Sr isochron was formed by variable degrees of mixing with fluid inclusions

Regarding the possible influence of fluid inclusions, Pettke and Diamond (1996) examined the relation between $^{87}\text{Sr}/^{86}\text{Sr}$ and reciprocal of Sr concentration for samples showing Rb–Sr isochrons. Figure 2 presents data for sphalerites from the Coy Mine using data from Nakai et al. (1990). Pettke and Diamond found that this type of plot shows no correlation indicative of mixing in the observed isochrons except for the sphalerites from the West Hayden ore body reported by Brannon et al. (1992). It can be concluded that Rb–Sr isochrons were not mixing lines between sphalerite residues and low Rb–Sr fluid inclusions except in this case. In addition, Christensen et al. (1995b) showed that Rb–Sr ratio in sphalerite residues from the Canning Basin was not controlled by Sr concentration negating the influence of fluid inclusions. They concluded that Rb incorporation into sulfide minerals during precipitation might be controlled kinetically.

Apart from MVT deposits, Shneider et al. (2007) compared Rb–Sr and Re–Os ages of ore-stage Zn–Cu–Ge sulfides, including sphalerite from the Kipushi base metal deposit, Democratic Republic of Congo. They respectively obtained concordant Rb–Sr and Re–Os ages of 451.1 ± 6.0 and 450.5 ± 3.4 Ma. The concordant ages further clarified the geological significance of direct Rb–Sr dating of sphalerites.

Rb–Sr Dating of Pyrite and Other Minerals

Apart from sphalerite, some other sulfide minerals have been found to be suitable for Rb–Sr dating. Tretbar et al. (2000) reported that Galkhaite $[(\text{Cs},\text{Tl})(\text{Hg},\text{Cu},\text{Zn})_6(\text{As},\text{Sb})_4\text{S}_{12}]$ from sedimentary-rock-hosted disseminated gold deposits known as Carlin-type gold deposits in Nevada formed a Rb–Sr isochron. The mineral shows high and variable $^{87}\text{Rb}/^{86}\text{Sr}$ ratios from 3,000 to 23,000. Pyrite has also been found to be a suitable mineral for Rb–Sr dating. Yang and Zhou (2001) dated pyrites from Linglong gold deposit, Jiaodong Peninsula, China. Yang and Zhou (2001) analyzed three sets of pure pyrite grains from three hand specimens of $6 \times 6 \times 9$ cm assuming that subsamples

from a single hand specimen are more likely to have a uniform initial Sr isotope composition. The three isochrons show concordant ages of 122 ± 11 , 122.7 ± 3.3 , and 123.0 ± 4.2 Ma. Wei et al. (2003) also applied Rb–Sr dating to pyrite from the Liaodong gold province, China.

Summary and Conclusions

Rb–Sr dating of sulfide minerals has been confirmed as a robust method for dating hydrothermal events. Because sulfide minerals contain only trace amounts of Rb and Sr, careful treatment of analyses is necessary. Combining Rb–Sr dating with other geochronometers such as Re–Os dating of sulfide minerals and Sm–Nd dating of scheelites is expected to shed light on details of ore formation processes of hydrothermal deposits.

Cross-References

- ▶ [Crustal Sulfide Minerals \(Re–Os\)](#)
- ▶ [Hydrothermal Events \(Sm–Nd\)](#)
- ▶ [Igneous Rocks \(Rb–Sr Geochronology\)](#)
- ▶ [Rb–Sr Dating](#)

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Stellar Chronology

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Synonyms

[Nuclear Cosmochronology](#); [Nucleocosmochronology](#)

Definition

Nucleocosmochronology. Use of radiogenic isotope ratios for determining ages of nucleosynthesis and other fractionations occurring in the galaxy and stars.

Introduction

Stars reflect the ongoing evolution of the galaxy as nuclidic abundances of metals (elements from carbon up in terms of proton number) are formed from the fusion reactions transforming light elements in to heavy. At the Fe abundance peak, fusion no longer releases energy, and elements heavier than iron are the result of two reaction pathways involving the addition of neutrons. The s-process involves the *slow* addition of neutrons, where slow indicates that the chances of beta decay is more likely than the chance of adding another neutron. The s-process therefore keeps the nucleosynthetic pathway close to the stable nuclides we see around us. The s-process stops at ^{209}Bi , this being the heaviest stable nuclide. The site of the s-process is likely dominated by asymptotic giant branch (AGB) stars, also known as red giants, that are burning He into heavier nuclides releasing abundant neutrons in the process.

The r-process denotes *rapid* addition of neutrons, so that many neutrons are added before a nuclide has a chance to decay. In the r-process, neutrons are added to quasi-stabilize nuclides far off the pathway of stability; once the neutron source is extinguished, the nuclides beta decay back to the canonical stable nuclides. The r-process therefore leads to much heavier nuclides being formed as the neutrons in the nucleus decay to protons. Uranium and thorium isotopes are therefore formed in this way. The astrophysical site of the r-process is likely to be supernova explosions resulting from core collapse as the density in the stellar core cannot resist gravitational contraction forming abundant neutrons in the process. These explosions take place over time periods of a few seconds with secondary nucleosynthesis (related to decay) on the order of months to years depending on the nuclide.

In terms of galactic chemical evolution, it is widely held that massive star formation was more prevalent in the early solar system, and hence r-process contributions are dominated by early galaxy supernovae explosions.

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Chronological Implication

It follows that nucleosynthesis itself could be dated if the initial abundances were known and the products could be measured. Theoretical models of r-process nucleosynthesis can be used to establish the abundances of uranium and thorium isotopes originating from that source. A classic case is that of the $^{235}\text{U}/^{238}\text{U}$ of our solar system first related in detail in the classic study of Willy Fowler and Fred Hoyle. The benefit of simply using uranium is that there is no inherent fractionation between the isotopes because of chemical processing. The isotope ratio is taken to simply reflect the decay of ^{235}U (half-life of 700 Myr) relative to ^{238}U (half-life of 4.4 Gyr). The r-process production (P) ratio $^{235}\text{U}/^{238}\text{U}$ is based on the contributions of not only $A = 235$ and $A = 238$ but also their respective α -decay progenitors up to $A = 255$ where spontaneous fission alone occurs; P235/P238 can be affected by details in r-process nucleosynthesis models. Fowler and Hoyle (1960) used a P235/P238U ratio of 1.65 in their calculations. The present day $^{235}\text{U}/^{238}\text{U}$ of our solar system is 0.00725, and the initial $^{235}\text{U}/^{238}\text{U}$ of the solar system is therefore 0.320 for the age of the solar system of 4.567 Gyr (Amelin et al. 2010). It follows then that

$$N^{235}/N^{238} = P^{235}/P^{238} e^{-(\lambda_{235}-\lambda_{238})t}$$

and the time t to evolve from a primitive r-process contribution to the time of the formation of our solar system is 2.0 billion years.

The Th/U ratio can also be used as a chronometer because of the difference in half-lives of ^{238}U and ^{232}Th . Here the calculation will also be affected by the potential for chemical fractionation of Th from U, which for the purposes of this calculation will be ignored. For the present Earth, the Th/U abundance is 3.6, and therefore 2.3 for the early solar system (Anders and Grevesse 1989). The r-process production ratio is around 1.7. Following a similar formalism to that above for uranium, the decay time is 2.8 billion years. Thus, the actinide abundances in the early solar system can be accommodated by injection of nucleosynthetic material that has been allowed to decay for 2–3 billion years.

However, the actinide abundances are being maintained in an equilibrium state balancing the nuclear decay with augmentation from new stellar explosions. Such a scenario is now supported additionally by the presence of short-lived radionuclides, many with half-lives less than 10 Myr such as the r-process nuclide ^{182}Hf . In accounting for this ongoing production and decay, Fowler and Hoyle derived an age of 15 (+5/–3) Gyr for the age of the galaxy, a remarkably prescient prediction.

Chronology from Stellar Abundances

For dating stellar systems other than our own, the ability to perform this kind of analysis is severely limited by our ability to measure the abundances of the nuclides in optical spectra. Isotopic analysis of heavy nuclides such as uranium is not possible. In fact detection of uranium is very difficult because of the coincidence of a CN (cyanide) line with U(II). Thorium is more promising to reflect age. The Th/Eu ratio can be used as a proxy for age because Eu is predominantly r-process and is a stable nuclide. The Th/Eu abundance will fall with time at a known rate because of the decay of ^{232}Th . As an example, the Th/Eu of the star CS 22892–052 is 0.219, well below the r-process ratio of 0.463, consistent with a simple radioactive decay age of 15.2 ± 3.7 Gyr.

These calculations assume simple single-stage decay models. Such a scenario is unlikely with a variety of stellar inputs likely making up the galactic abundances in any region of the galaxy.

Presolar grains are recovered from primitive meteorites, and these grains are believed to have condensed around stars that were extant before our solar system formed. Most of these appear to be derived from AGB stars with characteristic isotopic compositions from that source. Within single grains, U and Th are observed reflecting the ongoing r-process history of our galaxy.

Conclusion

The abundances of the radiogenic elements U and Th reflect ongoing processing in the galaxy. The abundances of these nuclides reflect billions of years of decay coupled with ongoing augmentation from supernovae.

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Uranium–Lead, Extraterrestrial, Planetary Materials

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Definition

From a broad perspective, extraterrestrial planetary materials comprise samples representing several identifiable planetary bodies in the solar system. The source planetary bodies can be identified with a high degree of confidence. Under a narrower definition used here, only samples originating from Moon and Mars are discussed.

Introduction

Extraterrestrial planetary materials available for study are restricted to a number of meteorite groups recovered mostly from deserts and Antarctic ice deposits on Earth, where meteorites are easily visible due to the significant contrast with the surrounding environment. These groups comprise several types of achondrites representing relatively small objects in the asteroid belt, SNC (Shergotty-Nakhla-Chassigny) meteorites believed to be originating from Mars and lunar meteorites. In addition, lunar materials have been made available by the Apollo and Luna missions that delivered around 380 kg of samples from nine locations on the near side of the Moon.

Many of the available samples contain U-bearing accessory minerals, such as zircon, zirconolite, tranquillityite, baddeleyite, apatite, and merrillite, allowing determination of U–Pb ages with the uncertainties of few million years. However, the relatively small abundance of these minerals in the samples, as well as the commonly restricted size of the samples, resulted in a limited number of analyses obtained prior to the advent of wide application of microanalytical techniques such as SIMS (secondary ion mass spectrometry) and LA ICPMS (laser ablation inductively coupled plasma mass spectrometry). Attempts to analyze U–Pb system in the whole rock samples or multigrain mineral separates using dissolution and chemical separation produced large errors due to the uncertainties associated with the unknown isotope composition of the non-radiogenic Pb component (i.e., Pb that is not formed from the in situ U decay) present in the samples. Nevertheless, recent application of intense leaching prior to dissolution of the samples helps to circumvent the problem and remove this non-radiogenic component, which often consists of a complex mixture of Pb incorporated into the samples during their formation or alteration or as contamination during the laboratory processing. Although leaching artificially separates Pb from U thereby reducing applicability of the system to ^{207}Pb – ^{206}Pb only, it does allow levels of accuracy and precision compatible with those obtained in the analysis of accessory minerals.

Development of analytical protocols combined with the improved understanding of behavior of U–Pb system in rocks and minerals resulted in an accelerated buildup of the chronological database of planetary materials during the last decade. This buildup helps to get a glimpse of geological

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processes operating in the solar system from its early evolutionary stages when magma differentiation and meteoritic bombardment influenced development of small bodies in the asteroid belt, Moon, and Mars to the very recent basaltic magmatism on Mars.

Although meteorites originating in the asteroid belt can be considered to represent early stages of planetary evolution and therefore treated as planetary materials, they are excluded from the discussion in this section, which concentrates on describing U–Pb systems in the rocks and minerals from the relatively large planetary bodies, Moon and Mars, each showing a prolonged history of magmatic evolution and differentiation.

U–Pb Ages of Lunar Samples

Two unique features of the Earth's Moon extend applicability of U–Pb system to the dating of materials that are often impossible to date in other terrestrial and extraterrestrial samples. The first one is the initial depletion of the Moon in Pb, which is attributed to the relative volatility of this element and its profound loss during the formation of the Moon. This loss results in a generally very high U/Pb observed in the majority of lunar materials, reducing influence of the initial Pb corrections required for the age calculations. This also makes it possible to extract coherent age information from usually difficult mineral phases such as apatite and even from volcanic and impact glasses, often showing very low U concentrations of 1–200 parts per billion (ppb). The second is a substantial enrichment of near side of the Moon in the incompatible elements, which stems from the final stages of crystallization of a global magma ocean on the Moon that formed a KREEP reservoir (for high concentration of K, rare earth elements (REE), and P). This results in an unusually high abundance of U-bearing minerals, including zircon in many lunar rocks, even those that are mafic in composition, which do not commonly host these minerals in non-lunar materials.

The contribution of U–Pb methods to the lunar chronology has to be viewed in the context of modern understanding of lunar history, which comprises several major stages following each other. This understanding was established utilizing a combination of different chronological, petrological, and geochemical techniques and suggests formation of the Moon as a result of a Giant Impact, which led to the lunar magma ocean that has determined initial differentiation of the planetary body and its subsequent magmatic evolution. Early plutonic magmatism was followed by extensive formation of mare basalts, which mostly subsided by about 3.0 Ga, with only few younger ages recorded in the available sample collection. In addition, the Moon as an airless body with very limited recent internal activity preserved evidence of meteoritic bombardment throughout its history. In particular, lunar exploration during the post-Apollo era has established the presence of a spike in the flux of impactors around 3.9 Ga, named the terminal lunar cataclysm.

Zircon is particularly abundant in the rocks of Mg and alkali suites formed as a result of a widespread plutonic magmatism on the Moon, which followed crystallization of the lunar magma ocean. These rocks range in composition from dunite and troctolite to gabbro-norite and anorthosite and probably formed as a result of differentiation of mafic magma inside the lunar crust by the processes similar to differentiation of layered intrusions on Earth. Some more felsic differentiates such as quartz-monzodiorite and granite are also present but substantially less common on the Moon. U–Pb dating of zircon from these rocks collected from several Apollo landing sites indicates multiple spikes of plutonic activity on the Moon between about 4.37 and 3.90 Ga (Meyer et al. 1996; Nemchin et al. 2008).

In addition to tracing the magmatic history of the Moon, lunar zircon grains often contain multiple features indicative of impacts. These features include planar deformation features (PDFs) and twins developed along specific directions in the crystals as well as deformed, recrystallized or amorphous domains present in the grains. Some of these internal structures are large enough to be dated using modern microanalytical methods and allow constraining ages of impacts. Importantly, the zircon U–Pb system is extremely stable even under very harsh conditions compared to the other radiogenic systems. As a result, unlike other systems that often record a substantial spike in the flux of impactors at about 3.9 Ga, zircon preserves a memory of much older impacts. At least two such impacts at about 4.35 and 4.20 Ga have been recognized based on the recent studies of lunar zircon (e.g., Pidgeon et al. 2007; Grange et al. 2009; Nemchin et al. 2009a).

Lunar phosphates represented by apatite and merrillite are common in both mare basalts and plutonic rocks. However, only in the latter do they appear to contain enough U to provide high quality age constraints. The earlier mentioned Pb depletion of the Moon makes lunar phosphates a much better target than similar minerals from other extraterrestrial and terrestrial materials. Nevertheless, only a limited number of U–Pb ages of lunar phosphates are published. These published results indicate a profound resetting of the system during the 3.9 Ga cataclysm (Grange et al. 2009; Nemchin et al. 2009b).

Rasmussen et al. (2008) demonstrated that at least some lunar basalts contain a suite of Zr minerals, such as zirconolite, tranquillityite, and baddeleyite. All these minerals also concentrate U in the quantities sufficient for a precise U–Pb dating. Although this initial work demonstrated the capability and opened the gateway for the investigation of ages of lunar basalts, only a few random studies of these minerals in lunar meteorites and Apollo breccia samples have been published during the following few years (e.g., Wang et al. 2012). A systematic study of U–Pb ages of accessory minerals in different types of lunar basalts from different landing sites remains one of the great opportunities for the future research.

In addition to mare basalts, late post-3.9 Ga basaltic volcanism on the Moon is represented by different types of volcanic glass beads accumulated in the lunar soils. These types are distinguished by their chemical compositions often indicating different source and depth of formation of parent melt in the lunar mantle. The glass beads are spherules varying in size from few microns to few millimeters and believed to be formed by lava fountaining into space, resulting in the dispersion of melt and formation of spherical droplets, which solidify and settle downwards accumulating in the lunar regolith. Nemchin et al. (2011, 2013) showed that some of these glasses contain a very small proportion of initial Pb and enough U to provide meaningful ages, opening yet another avenue to study lunar basaltic magmatism. The general spread of ages between about 3.8 and 3.0 Ga was constrained for both mare basalts and volcanic glasses following the sample returns by Apollo missions. However, development of new microanalytical methods opens an opportunity to investigate detailed distribution of ages of different types of basalts on the Moon with unprecedented temporal resolution utilizing advantages given by the U–Pb system, such as its general stability in many minerals even under severe conditions during secondary events and capability to test internal consistency using two independent decay schemes (i.e., ^{238}U to ^{206}Pb and ^{235}U to ^{207}Pb).

One major component of the lunar rock suite identified by the investigation of samples in the Apollo collection, which appears not to be suitable for U–Pb dating using a microanalytical approach, is a set of ferroan anorthosites (FAN) comprising the crust of the Moon. These anorthosites commonly contain just a few percent of mafic minerals and no U-bearing accessory phases restricting applicability of U–Pb dating methods. Multiple attempts to determine U–Pb ages of these rocks using whole rock samples and mineral separates were hindered by the presence of multiple non-radiogenic Pb components. However, recent study of a FAN sample from Apollo 16

landing site (Borg et al. 2011) utilized heavy leaching of the separates prior to their dissolution for analysis and was able to quantitatively remove these components, achieving precise age estimate of 4359.2 ± 2.4 Ma from the $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ isochron. This age is similar to Sm–Nd age obtained from the same separates increasing confidence that it is a true age of the sample.

U–Pb Ages of Martian Samples

Martian samples are less abundant than lunar materials and restricted to basalts and mafic-ultramafic cumulates. Detailed imaging of the Martian surface by orbiters indicates significant difference in elevation and composition of northern and southern hemisphere. This dichotomy is also expressed in the substantial difference in the observed crater density and hence the age. The southern hemisphere called the southern highlands is heavily cratered and ancient. In contrast the lowlands of northern hemisphere show very few large craters and appear to be much younger. It is believed that majority of available Martian Shergotty-Nakhla-Chassigny (SNC) meteorites originate from this younger part of the planet.

Analysis of various isotope systems in whole rocks and mineral fractions of SNC meteorites resulted in a general agreement that nakhlites and chassignites are ~1.3 Ga old and shergottites are significantly younger in the order of a few hundred million years (e.g., Nyquist et al. 2001). However, U–Pb or rather Pb–Pb systematics of one SNC group, basaltic shergottites, became a subject of ongoing controversy. Most mineral isochrons obtained by different isotope techniques cluster around 180 and 330–475 Ma (Nyquist et al. 2001). However, in $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates, data for a number of these samples form arrays, interpreted by Bouvier et al. (2005, 2008) as isochrons, defining ages close to 4.0–4.1 Ga. Consequently two conflicting interpretations of U–Pb system in basaltic shergottites have coexisted in the literature for almost a decade. One interpretation advocates a young time of formation for these rocks (e.g., Nyquist et al. 2001; Borg et al. 2005; Borg and Drake 2005) and explains unusually old Pb–Pb ages of shergottites as a feature inherited from the basaltic magma source that differentiated very early in Martian history. The other (Bouvier et al. 2005 and 2008) interprets these old ages as true ages of the rocks, finding additional evidence for this conclusion in the studies of cratering of Martian surface. These studies suggest a very small fraction of young terrains on Mars, creating a conflict if shergottites are young and present in a high proportion among the available Martian meteorites. Within this point of view, younger ages of basaltic shergottites obtained using other isotope systems reflect resetting of these systems during the impacts, probably those that ejected meteorites from Mars and set them on the collision course with Earth.

Several studies attempted to resolve this controversy by U–Pb dating of baddeleyite often present in shergottites and formed during the magmatic crystallization of the rocks. Zhou et al. (2013) reported $^{206}\text{Pb}/^{238}\text{U}$ age of 182.7 ± 6.9 Ma for baddeleyite from the Zagami meteorite, while Moser et al. (2013) investigated baddeleyite crystals overgrown by the submicron zircon grains from meteorite NWA5298. This zircon was interpreted as forming as a result of reaction between baddeleyite and high-Si fluid or melt generated during the impact that launched this meteorite into the space. The $^{206}\text{Pb}/^{238}\text{U}$ ages of baddeleyite grains investigated in this study spread between 227 ± 18 and 22 ± 2 Ma, giving both time of baddeleyite crystallization, estimated as 187 ± 33 Ma on the basis of the least disturbed grains, and an upper limit for the impact event given by the youngest baddeleyite analysis (Moser et al. 2013). Consequently, published results of U–Pb baddeleyite dating appear to support the young age of basaltic shergottites.

One of two samples that are different from the main population of rocks in the Martian meteorite collection is orthopyroxenite ALH84001. The sample is composed of 96 % orthopyroxene, a composition unusually uniform for Martian meteorites (Mittlefehldt 1994), and some minor chromite, plagioclase, and phosphate. In addition carbonates with strong compositional zoning are found along the fractures and cataclastic areas. Difference of this sample from all other known Martian meteorites is also supported by the consistently ancient age obtained from all isotope systems (Nyquist et al. 2001). Even Rb–Sr and K–Ar (^{39}Ar – ^{40}Ar) systems, which are most prone to resetting, show ages that are not younger than 3.9 Ga. Although, the silicate constituents of ALH84001 are not possible to date using U–Pb system, Borg et al. (1999) utilized compositional variability of carbonates in these samples to obtain a 4.04 ± 0.1 Ga age from the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ isochron. This is similar within the errors to the Rb–Sr age of 3.90 ± 0.04 Ga, supporting an ancient formation age of its carbonates.

The second set of samples distinct from SNC is represented by paired meteorites NWA7533 and NWA7034 recently identified as originating from Mars (Agee et al. 2013). Humayun et al. (2013) described these rocks as a regolith breccia formed as a result of impact or series of impacts that collected a variety of fragments of different origin near the Martian surface and fused them together with the interstitial impact melt. Mineral and chemical composition of the fragments and the samples suggest that these meteorites are the first available samples from southern hemisphere of Mars. This is supported by the age of zircon grains identified in these samples and associated with the group of leucocratic, K-feldspar-rich clasts. Humayun et al. (2013) reported results of U–Pb dating of these zircons. Several analyzed grains are concordant defining a crystallization age of zircon grains (and their host rocks) as $4,428 \pm 25$ Ma. Others fall on a discordia with the upper intercept age similar to that of concordant zircon and the lower intercept defining the time of resetting of U–Pb system in the most metamict grains as $1,712 \pm 85$ Ma.

Summary or Conclusions

Development of microanalytical methods of isotope analysis allowing in situ age determination in the small (few tens of micrometers) areas inside individual grains resulted in significant expansion of U–Pb age database of planetary materials, which include lunar and Martian samples. Combined with detailed imaging of the samples, these ages give unprecedented new information about the origin and evolution of the planets and have direct and indirect influence on the development of ideas and models for evolution of our own planet Earth. A variety of planetary materials of diverse composition and origin can be dated using U–Pb system, as U is concentrated in the quantities sufficient for analysis in a number of different minerals and glasses. Some of these materials, such as zircon in lunar breccias, have been extensively studied during the last decade, while capability of others remain mostly unexplored leaving a significant potential for the future research and new discoveries.

Cross-References

- [Apatite](#)
- [Lutetium–Hafnium Dating](#)
- [Mass Spectrometry](#)
- [Meteorite Impacts](#)

- Moon Formation
- Potassium–Argon (Argon–Argon), Extraterrestrial Materials
- Potassium–Argon and Argon–Argon Dating
- Radiation Dose Rate
- Rubidium–Strontium Dating
- Samarium–Neodymium Dating
- Secondary Ion Mass Spectrometer (SIMS)
- Thermal Ionization Mass Spectrometer (TIMS)
- Uranium–Lead Dating
- Uranium–Lead, Zircon
- Zircon

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Early Life on Earth

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Definitions

The most obvious signs of early life on Earth are in the form of *body fossils*. On the early Earth, only the most primitive of microorganisms lacking any hard parts would have been present, so only soft parts in the form of cells, sheaths, and perhaps associated secreted polymeric substances are likely to be found. Alternatively, signs of life may be in the form of *trace fossils*. These are nonbody remains that in the broadest sense indicate the activity of an organism (e.g., a microboring) or a community of organisms (e.g., a stromatolite or microbially induced sedimentary structure). A third way early life may be recognized is in the form of *chemical fossils*. These are traces of biological activity indicated by specific chemical signals left in rocks. Chemical fossils may be preserved in organic matter or in “biominerals” such as pyrite; they include isotopic variations in carbon, sulfur, nitrogen, or iron, distinctive ratios of elements, or molecular compounds that may be tied to a particular group of organisms.

Protocols for Identifying Early Life on Earth: Where to Look

This is not merely a case of looking at Earth’s oldest rocks. As well as being demonstrably of the correct age, such rocks must have been deposited in a setting that could viably host life and ideally should have undergone minimal postdepositional alteration. When these factors are taken into consideration, the search for Earth’s earliest life is focused on two main areas of the world: the Pilbara Craton of Western Australia and the Barberton greenstone belt of southern Africa, both containing sedimentary and volcanic rocks up to c. 3.5 billion years old (Ga [giga-annum]). In addition, parts of Greenland contain putative sedimentary rocks approaching 3.8 Ga, but these have been altered (metamorphosed) at higher temperatures and strain rates making the identification of life more difficult and controversial.

Protocols for Identifying Early Life on Earth: Establishing Antiquity

Proving that a putative life signature is of undoubted early Archean (i.e., >c. 3 Ga) age is a vital step in testing any claim for Earth’s earliest life. Hence, a number of antiquity criteria have been put forward that any life sign should satisfy. These include being able to demonstrate the age and provenance of the host rocks, that the candidate life sign is both physically embedded within the host rock (indigenous) and not introduced by later fluids (syngenetic), and that it has a composition (carbonaceous or non-hydrated mineral) and color (i.e., black to dark brown if carbonaceous)

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consistent with the deposition and alteration history of the host rock (see Wacey 2009, for detailed criteria).

Protocols for Identifying Early Life on Earth: Establishing Biogenicity

Criteria have also been put forward to minimize the possibility of interpreting a nonbiological structure as biological. Thus, candidate microfossils should exhibit the following: biological morphology that can be related to extant cells, sheaths, or waste products; more than a single step of biology-like processing, perhaps in the form of associated biominerals, geochemical fractionations of isotopes, specific organic compounds, or distinctive elemental ratios; a geological and evolutionary context that is plausible for life; abundance, ideally occurring in a multicomponent assemblage showing community behavior; kerogenous carbon composition or composed of microbially mediated minerals such as pyrite; a largely hollow nature and occupying a restricted biological morphospace; evidence for taphonomic degradation such as collapse of cells, folding of films, or fracturing; and dissimilarity from known potentially coexisting nonbiological organic bodies (e.g., self-organizing spherulitic structures).

Similarly, trace fossils such as microbial borings should exhibit the following: circular to elliptical cross sections and a restricted range of diameters; preferential exploitation of certain substrates or horizons; enrichments of biologically important elements, such as carbon and/or nitrogen enriched linings, or biomineral infillings; and preferred growth orientations. Stromatolites must also fulfill a set of criteria in an attempt to exclude abiotic mimics such as soft sediment deformation, later structural deformation, and chemical precipitation of stromatolite-like crusts (see Wacey 2009, for detailed criteria).

Protocols for Identifying Early Life on Earth: Techniques

Fulfilling the criteria outlined above requires the use of a wide range of techniques that permit investigation from the kilometer to nanometer scale. Geological mapping at scales from kilometers to meters, supported by mapping of petrographic thin sections (c. 30–100 μm -thick rock slices), is required to show that candidate life structures are truly syngenetic and ancient. This contextual and petrographic mapping is also the first stage in falsifying the null hypothesis of a nonbiological origin for a given object.

Obtaining evidence for a uniquely biological morphology requires in situ imaging and mapping of morphospace to distinguish the fields of biological and nonbiological morphology and to compare these with self-organizing structures. This is commonly undertaken under the optical microscope using petrographic thin sections but with recent technological advances may also extend to investigation using a scanning electron microscope (SEM), transmission electron microscope (TEM), lasers, or X-rays. One recent advance is the ability to extract site-specific ultrathin (c.100 nm) wafers from a petrographic thin section or rock chip using a focused ion beam (FIB), allowing the morphology of candidate life signs to be studied at nanometer-scale spatial resolution in the TEM. FIB combined with SEM also permits 3D modeling and reconstruction of candidate microfossils at nanometer-scale resolution. Laser Raman microspectroscopy and X-ray tomography also permit visualization of candidate microfossils in 3D albeit at poorer spatial resolution.

Finally, obtaining geochemical evidence for metabolic cycling requires micro- to nanoscale in situ mapping and analysis. Here, potential biological isotope fractionations can be detected using

Table 1 Summary of reported evidence for life in >3 Ga rocks in the Pilbara region of Western Australia

Age	Geological unit	Morphological evidence	Geochemical evidence	References
~3 Ga	Farrel Quartzite, Gorge Creek Group	Microfossils: spheroids, 2.5–80 µm in diameter; lens/spindle shapes up to 40 µm in length and 35 µm in width; threadlike filaments <1 µm diameter and up to 100 µm in length; potential carbonaceous biofilms (see Fig. 1j)	Bulk carbon isotopes: $\delta^{13}\text{C}$ c. –30 ‰ to –35 ‰ consistent with biology Laser Raman: fossils are made of carbon and carbon structure is consistent with age and biology Elemental mapping: C, N, and S found in microfossil walls	Sugitani et al. 2009
~3.24 Ga	Kangaroo Caves Formation, Sulfur Springs Group	Microfossils: solid pyritic filaments 0.5–2 µm in diameter and up to 300 µm in length, often intertwined and densely clustered (see Fig. 1h) Microfossils: filaments and tubes <1 µm wide, often bundled in packages 1–5 µm in diameter and up to 100 µm in length; aggregates of tiny spheres <50–100 nm in diameter	None Bulk carbon isotopes: $\delta^{13}\text{C}$ c. –27 ‰ to –34 ‰ consistent with biology	Rasmussen 2000 Duck et al. 2007
~3.35 Ga	Euro Basalt, Kelly Group	Trace fossils: microtubes 1–5 µm in diameter and up to 150 µm in length, often branched and segmented Microfossils: spheroids c. 8 µm in diameter; spheroids c. 21 µm in diameter sometimes enclosed by a potential sheath	Elemental mapping: possible enrichments of C and N within the microtubes None	Banerjee et al. 2007 Schopf and Packer 1987
~3.4 Ga	Strelley Pool Formation	Microfossils: carbonaceous spheroids (c. 5–25 µm in diameter), tubes (c. 7–20 µm in diameter), and rare cellular envelopes (up to 80 µm in diameter), associated with micron-sized pyrite. Spheroids often cluster and organize into chains. Microfossils colonize sand grains and some show taphonomic degradation (see Fig. 1f) Stromatolites: best examples are conical and columnar morphologies with trapped and reworked grains (see Fig. 1d) Microfossils: lenticular/spindle shapes (long axis c. 35–120 µm), large spheroids (up to c. 100 µm diameter), clusters of smaller spheroids, wrinkled and folded carbonaceous films, and threadlike filaments	In situ carbon isotopes: $\delta^{13}\text{C}$ –33 ‰ to –46 ‰ consistent with biology In situ sulfur isotopes: $\delta^{34}\text{S}$ range of 18 ‰ and $\Delta^{33}\text{S}$ of +1.43 ‰ to –1.65 ‰ indicating sulfur-processing metabolisms Elemental mapping: nitrogen enrichment in microfossil walls Laser Raman: carbon structure consistent with age and biology Elemental distributions: co-occurrence of C, N, and S in detrital carbonaceous grains; rare earth element enrichment in carbonate laminae relative to chert laminae is consistent with younger microbial carbonates Bulk carbon isotopes: $\delta^{13}\text{C}$ c. –31 ‰ to –37 ‰ consistent with biology Laser Raman: shows microfossils are carbonaceous and carbon has structure consistent with age and biology	Wacey et al., 2011a Allwood et al. 2006 Sugitani et al. 2010

(continued)

Early Life on Earth, Table 1 (continued)

Age	Geological unit	Morphological evidence	Geochemical evidence	References
		Trace fossils: microborings (channels and spherical to elliptical surface pits, with near constant diameter of 1–5 μm) often concentrated in clumps along one side of a detrital pyrite grain (see Fig. 1e)	Elemental mapping: C and N enrichments in some microborings Laser Raman: shows carbonaceous biofilms associated with some microborings; carbon has structure consistent with age and biology	Wacey et al., 2011b
		Possible trace fossils: microtubes containing a pyrite grain at their termination – known as ambient inclusion trails	In situ carbon isotopes: mean $\delta^{13}\text{C}$ of c. –26 ‰ from carbonaceous microtube linings Elemental mapping: enrichments in C, N, P, and S in some microtubes	Wacey et al. 2008
~3.45 Ga	Panorama Formation, Warrawoona Group	Microbial mat with microfossils: spheroids (<1 μm in diameter), often clustered or in chains; filaments (<1 μm diameter and up to 40 μm in length); occasional rod shapes; films interpreted as fossilized extracellular polymeric substances (see Fig. 1c)	Bulk carbon isotopes: $\delta^{13}\text{C}$ c. –26 ‰ to –30 ‰ consistent with biology Laser Raman: spectra indicate carbon with a structure consistent with age and biology	Westall et al. 2006b
~3.46 Ga	Apex Basalt, Warrawoona Group	Possible microfossils: filaments – eleven “species” varying in average diameter from 0.5–16.5 μm and 28–89 μm in length BUT: many are C-, J-, and L-shaped structures around spherulitic silica crystals; some follow ghost rhombic crystal outlines	Bulk carbon isotopes: $\delta^{13}\text{C}$ averages –27.7 ‰ consistent with biology Laser Raman: spectra show objects are made of carbon and structure consistent with biology BUT: carbon isotope and Raman signals are also consistent with abiotic carbonaceous artifacts; some may not be carbonaceous	Schopf 1993 Brasier et al. 2002
~3.49 Ga	Dresser Formation, Warrawoona Group	Microfossils: 3 types of filaments: (a) average 1 μm in diameter, some mutually interwoven and branched; (b) segmented, unbranched, average 8.7 μm in diameter; (c) non-segmented, tubular, average 12.6 μm in diameter Stromatolites: coniform, nodular, domical and wavy-laminated morphotypes (see Fig. 1a) Microfossils: entire “hollow cells” and fragments such as “cell walls” observed under the transmission electron microscope Possible biominerals: microscopic pyrite (no biological morphology) Methane in fluid inclusions: no biological morphology	Bulk and in situ carbon isotopes: $\delta^{13}\text{C}$ c. –30‰ to –42 ‰ consistent with biology None Bulk carbon isotopes: $\delta^{13}\text{C}$ c. –32 ‰ to –36 ‰ consistent with biology Bulk and in situ sulfur isotopes: $\delta^{34}\text{S}$ range of 22‰; $\Delta^{33}\text{S}$ of +6 ‰ to –1.2 ‰ consistent with sulfur-processing biological metabolisms Carbon isotopes: $\delta^{13}\text{C}$ –36 ‰ to –56 ‰ consistent with microbial methanogenesis	Ueno et al. 2001 Van Kranendonk et al. 2008 Glickson et al. 2008 Shen et al. 2009 Ueno et al. 2006

Table 2 Summary of reported evidence for life in >3 Ga rocks in the Barberton region of South Africa

Age	Geological unit	Morphological evidence	Geochemical evidence	References
~3.22 Ga	Moodies Group	Microbially induced sedimentary structures: wrinkle and roll-up structures; aligned grains in a matrix of carbonaceous laminae (see Fig. 1i)	Bulk carbon isotopes: $\delta^{13}\text{C}$ around -20‰ consistent with biology	Noffke et al. 2006
~3.25 Ga	Fig Tree Group	Stromatolites: laterally linked domes, pseudo-columns, and crinkly stratiform varieties	None	Byerly et al. 1986
		Putative microfossils: spheroidal 1–4 μm in diameter; possible internal contents; possible binary division	None	Knoll and Barghoorn 1977
~3.3–3.4 Ga	Kromberg Formation, Onverwacht Group	Microbial mat: carbonaceous laminations with portions “ripped up” and/or folded over; some filaments preserved (see Fig. 1g)	Bulk carbon isotopes: $\delta^{13}\text{C}$ of -25‰ to -35‰ consistent with biology	Tice and Lowe 2004
		Carbonaceous grains: possible eroded fragments of a microbial mat	Bulk carbon isotopes: $\delta^{13}\text{C}$ of -25‰ to -35‰ consistent with biology	Tice and Lowe 2004
		Putative microfossils: a selection of <2 μm spheroidal and rodlike morphologies, often clustered or paired	Bulk carbon isotopes: $\delta^{13}\text{C}$ of -27‰ consistent with biology	Westall et al. 2001
		Putative microfossils: tubular and solid carbonaceous and pyritic filaments up to 2.5 μm diameter and 200 μm long, plus large spindle shapes	None	Walsh 1992
~3.45 Ga	Hoogenoeg Formation, Onverwacht Group	Trace fossils: segmented microtubes ~ 4 μm in diameter and up to 200 μm in length (see Fig. 1b), plus clustered spheres	In situsulfur isotopes: $\delta^{34}\text{S}$ of -40‰ to -3‰ from pyrite in microtubes indicates sulfur-based metabolism	McLoughlin et al. 2012
			Bulk carbon isotopes (carbonate): $\delta^{13}\text{C}$ of -16‰ to $+4\text{‰}$	Furnes et al. 2004
		Putative microfossils: solid filaments up to 2.6 μm diameter and 200 μm long	None	Walsh and Lowe 1985
		Putative microfossils: sausage-shaped, up to 3.8 μm long and 1.1 μm wide	None	Westall et al. 2006a
		Putative microbial mat: crinkly carbonaceous laminations; some bundled, broken, or folded over; carbonaceous grains	None	Walsh 1992
		Microbial mat: comprising parallel and interwoven filaments; mat was flexible	Bulk carbon isotopes: $\delta^{13}\text{C}$ of -23‰ consistent with biology	Westall et al. 2006a

secondary ion mass spectrometry (SIMS); high sensitivity and high spatial resolution elemental mapping can be performed using NanoSIMS, TEM, or synchrotron. The structure of carbon or

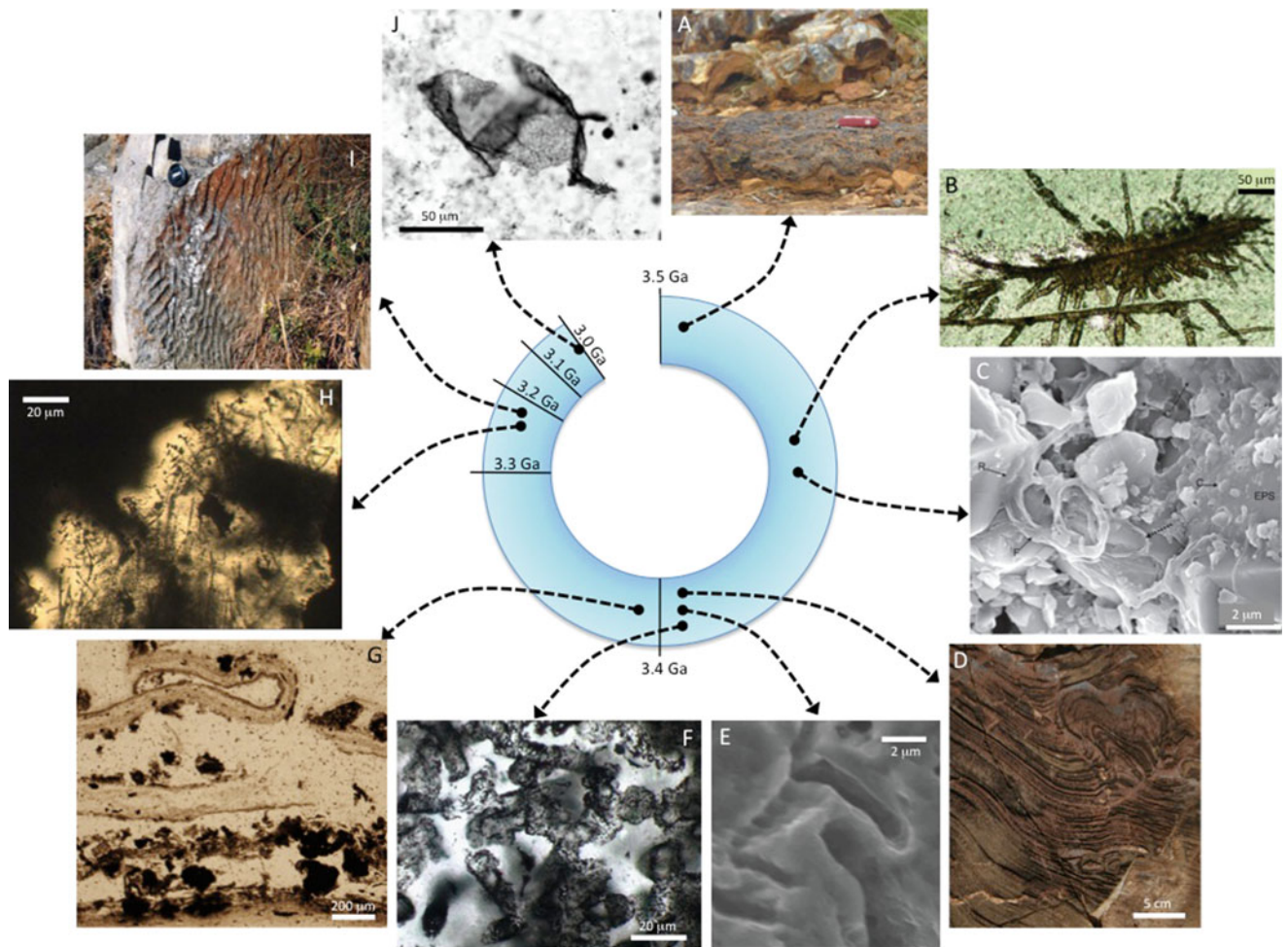


Fig. 1 Examples of early life on Earth. (a) Wavy-laminated and domical stromatolites from the c. 3.49 Ga Dresser Formation, Australia (Penknife for scale; photo courtesy of M. van Kranendonk). (b) Microtubular structures interpreted as endolithic trace fossils from the outer margin of a pillow basalt from the c. 3.45 Ga Hoogenoeg Formation, South Africa (Photo courtesy of N. McLoughlin and reproduced under the fair usage policy of the Geological Society of America). (c) Filaments (*f*), rods (*r*), coccoids (*c*), and possible extracellular polymeric substances from the c. 3.45 Ga Panorama Formation, Australia (Photo reproduced from Westall et al. 2006b, under the fair usage policy of the Geological Society of America). (d) Complex stromatolite from the c. 3.4 Ga Strelley Pool Formation, Australia (Photo by author). (e) Microbial trace fossils within pyrite from the c. 3.4 Ga Strelley Pool Formation (Modified from Wacey et al. 2011b). (f) Tubular microfossils from the c. 3.4 Ga Strelley Pool Formation (Photo by author). (g) Carbonaceous grains and folded microbial mat from the c. 3.4 Ga Kromberg Formation, South Africa (Photo by author). (h) Putative filamentous microbes preserved in pyrite from the c. 3.24 Ga Kangaroo Caves Formation, Australia (Photo by author). (i) Microbially induced sedimentary structures (*MISS*) from the c. 3.22 Ga Moodies Group, South Africa (Camera lens cap for scale; photo courtesy of N. Noffke). (j) Folded and torn biofilm from the c. 3.0 Ga Farrel Quartzite, Australia (Photo courtesy of K. Sugitani)

more complex organic material can be investigated using laser Raman microspectroscopy, TEM, or synchrotron, and the oxidation and bonding states of some biologically important elements such as Fe and S can also be resolved using TEM or synchrotron (see Wacey 2009, 2012, for details on techniques).

Examples of Earth's Earliest Life

Reported examples of > 3 Ga life on Earth are summarized in Tables 1 and 2, plus Fig. 1.

Summary

Possible signs of life have been reported from eleven separate geological formations and from at least eight different lithologies in the Pilbara and Barberton regions, spanning almost the entire exposed 3–3.5 Ga stratigraphy. Evidence for life includes stromatolites, microfossils, trace fossils, biominerals, and isotopic signatures and comes from environments as diverse as a carbonate platform, sandy beach, and deep-sea hydrothermal black smoker. Putative life signals, in the form of isotopic signatures, have also been reported from rocks as old as c. 3.8 Ga in Greenland but these are particularly controversial.

Cross-References

- ▶ [Chert](#)
- ▶ [Earth's Oldest Rocks](#)
- ▶ [Isua Greenstones](#)
- ▶ [Mass Spectrometry](#)
- ▶ [Molecular Clocks, Evolutionary Events](#)
- ▶ [Quartz](#)
- ▶ [Stromatolite](#)

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Groundwater Dating with Atmospheric Halogenated Compounds

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Synonyms

CFC dating; Chlorofluorocarbon dating; SF₆ dating

Definition

Atmospheric environmental releases refer to the emission of stable, long-lived compounds of solely anthropogenic origin into the atmosphere and the use of the compounds to estimate dates of their incorporation into groundwater.

Introduction

The majority of environmental anthropogenic tracers that can be used to date groundwater were released to the atmosphere after 1940 (Fig. 1). Groundwater dating relates the measured concentration of these trace atmospheric gases to the reconstructed history of the trace gas concentration in the atmosphere. Three general types of tracers can be used to date groundwater: (1) halogenated tracers, including the chlorofluorocarbons and hydrochlorofluorocarbons (CFCs and HCFCs), the perfluorocarbons and hydrofluorocarbons (PFCs and HFCs), sulfur hexafluoride (SF₆), trifluoromethyl sulfur pentafluoride (SF₅CF₃), and nitrogen trifluoride (NF₃) (IAEA 2006); (2) anthropogenic radiogenic tracers introduced by atmospheric nuclear testing and reactor fuel reprocessing (³H, ¹⁴C, ³⁶Cl, and ⁸⁵Kr) (Cook and Herczeg 1999; Plummer 2005); and (3) event markers which include alkylbenzene sulfonate (ABS) and linear alkylbenzene sulfonate (LAS) surfactants, herbicides, pharmaceuticals, pesticides, and their degradation products (Plummer et al. 1993). A number of excellent reviews discussing groundwater ages and dating methods using environmental tracers have been published (Plummer et al. 1993; Cook et al. 1995; Plummer and Friedman 1999; Goode 1996; Höhener et al. 2003; Bethke and Johnson 2008; Darling et al. 2010; Newman et al. 2010). This section discusses the application of halogenated atmospheric tracers to groundwater dating.

CFCs were first synthesized in the late 1920s, and by the 1940s they became the replacements for ammonia, sulfur dioxide, and methyl chloride as refrigerants, which had been implicated in a series of accidents and deaths (Giunta 2006). CFC production, applications, and releases accelerated after World War II, with chlorofluorocarbons eventually comprising approximately half of the tropospheric chlorine burden (Schauffler et al. 1993). In developed countries, production of CFCs stopped, and releases slowed following ratification of the *Montreal Protocol on Substances that Deplete the Ozone Layer* treaty. Concentrations in the atmosphere are now in decline (WMO 2010). The CFCs have been replaced by hydrochlorofluorocarbons (HCFCs), which will also be phased out by 2030, and by hydrofluorocarbons (HFCs). These compounds have much shorter atmospheric

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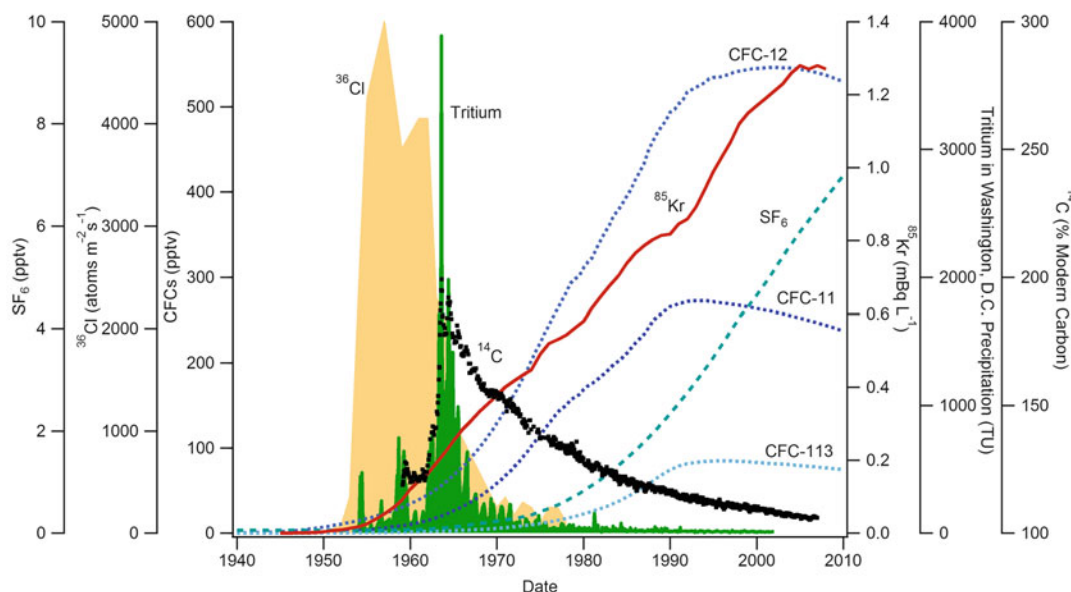


Fig. 1 Historic northern hemisphere background air concentrations of CFC-11, CFC-12, CFC-113, and SF₆ (<http://water.usgs.gov/lab>); global average ⁸⁵Kr activity per liter of air (Ahlsweide et al. 2009, 2013); northern hemisphere ³⁶Cl deposition rate (Bentley et al. 1986; Bentley et al. 1982; Althaus et al. 2009); ³H activity in Washington, DC, precipitation (IAEA/WMO 2006); and global average percent modern ¹⁴C in atmospheric CO₂ (Nydal and Lövseth 1983; Winger et al. 2005; Turnbull et al. 2007)

lifetimes and are less damaging to the ozone layer than the CFCs (WMO 2010). The concentration of perfluorocarbons (PFCs) (CF₄, C₂F₆), SF₆, and SF₅CF₃ are lower than CFCs, have atmospheric lifetimes of hundreds to thousands of years, and are potent greenhouse gases (IPCC 2007). PFC analysis in water is difficult and these compounds have not been routinely used in groundwater dating (Deeds et al. 2008; Deeds 2008). In contrast, analyses of CFCs, SF₆, and SF₅CF₃ are relatively easy by gas chromatography with an electron capture detector (GC-ECD) (Lovelock 1958, 1974; Thompson and Hayes 1979; Busenberg and Plummer 1992; Bullister and Weiss 1988; Hofer and Imboden 1998; Busenberg and Plummer 2000, 2008).

Dating young groundwater is important for evaluating groundwater resources. CFC dating was used to obtain the historical record of nitrate contamination in aquifers (Böhlke and Denver 1995; Katz et al. 2001; Lindsey et al. 2003; Böhlke et al. 1997; Johnston et al. 1998) and groundwater pollution histories and evaluation susceptibility of aquifers to contamination (Shapiro et al. 2004; Nelms et al. 2003; Plummer et al. 2008), to evaluate aquifer resources (Dunkle et al. 1993; Szabo et al. 1996; Plummer et al. 2000; Bauer et al. 2001; Burton et al. 2002; Lindsey et al. 2003; Cook et al. 2005; Gooddy et al. 2006; McMahon et al. 2011; Manning et al. 2012; Liu et al. 2013; von Rohden et al. 2010b), and to calibrate groundwater models (Reilly et al. 1994; Weissmann et al. 2002).

Groundwater Dating Theory

The concentrations of environmental tracers in groundwater are affected by transport processes. Dating based on concentrations of atmospheric gases in groundwater depends on the model used and model-dependent assumptions of mixing and transport in aquifers. For preliminary age interpretations, the piston-flow model is used (Fontes 1982; Zuber 1986). The piston-flow dating method uses

the measured tracer concentrations in water and their calculated partial pressures and subsequently compares them to known historical concentrations in the atmosphere. Several assumptions are implied by the piston-flow model: the tracers are in equilibrium with the gas at the water table during recharge (when the water reaches the water table), the tracer partial pressures at the water table are the same as the atmosphere (i.e., the unsaturated zone is less than 10 m thick), the recharge temperature and elevation are known, and the tracer concentrations in the aquifer were not significantly modified by adsorption, contamination, matrix diffusion, or biodegradation. The piston-flow model assumes that water moves as closed packets with no mixing or hydrodynamic dispersion (Fontes 1982). The concentration of several environmental tracers in groundwater can also be described by lumped-parameter mathematical models. These models use simplified aquifer geometries, flow, hydrodynamic dispersion, and mixing to describe tracer concentrations in the aquifer and borehole (Zuber 1986; Zuber and Rosanski 2007; Cook and Böhlke 1999; Gooddy et al. 2006; Eberts et al. 2012; Jurgens et al. 2012). However, groundwater samples are mixtures of packets of molecules each with a unique age and tracer concentration. This is an important distinction, as individual components have different aquifer residence times. Thus, a successful reactive transport flow model will calculate all the observed tracer concentrations in the groundwater. Tracer concentrations are best used to calibrate transport and flow models which can be used to determine the average residence time of the sample in the aquifer (Etcheverry and Perrochet 2000; Bethke and Johnson 2008; Newman, et al. 2010).

Uncertainty in age determination (disparities between tracers ranging from several to many years) can derive from many sources, including vadose zone thickness, recharge temperature, infiltration rate, dispersion, mixing, and bacterial activity (IAEA 2006). Corrections need to be applied to tracer concentration measurements if recharge is through thick unsaturated zones since the partial pressures at the water table can be significantly different from atmospheric concentrations due to diffusion through the vadose zone (Cook et al. 1995, 2006; Cook and Solomon 1997, Busenberg and Plummer 2000, 2008; Engesgaard et al. 2004). The recharge temperature may be different from the water temperature at the time of sampling, since recharge temperature is often within ± 1 °C of the mean annual air temperature of the recharge area (Collins 1925; Zuber et al. 1995; Stute and Schlosser 1993). Tracer concentrations will exceed the equilibrium concentration when there is a rapid rise in the water table, which causes trapped gas bubbles (excess air) to dissolve due to the increase in hydrostatic pressure and which requires correction of the dissolved tracer concentrations (Stute et al. 1995; Aeschbach-Hertig et al. 1999, 2000; Sun et al. 2010). The recharge temperature, excess air, and recharge elevation can be estimated from dissolved noble gas concentrations (Ne, Ar, Kr, and Xe) measured by mass spectrometry (Cook et al. 2006; Sun et al. 2010). In aerobic waters, the recharge temperature and excess air can be estimated by gas chromatography (GC) from the concentrations of N₂ and Ar alone (Heaton and Vogel 1981).

Relationships Between Age Tracers and Solubility

The equilibrium concentration of gases in water is described by Henry's Law (Eq. 1), which equates the aqueous concentration to the partial pressure (mole fraction) of gases above the water:

$$C_w = K_h(x_i) \quad (1)$$

where C_w is the molar concentration of the gas in water, K_h is the Henry's Law constant, and x_i is the partial pressure of the gas (Weiss 1970; Warner and Weiss 1985). The equilibrium concentration is

Table 1 Solubility coefficients to the Clarke-Glew-Weiss (Eq. 4) used for determining solubilities in water (Warner and Weiss 1985; Bu and Warner 1995; Bullister et al. 2002; Busenberg and Plummer 2008). Units are in mol L⁻¹ atm⁻¹

Compound	A	B	C	D	E	F	Ref.
CFC-11 (CCl ₃ F)	-134.1536	203.2156	56.2320	-0.144449	0.092952	-0.015997	(Bullister and Weiss 1988)
CFC-12 (CCl ₂ F ₂)	-122.3246	182.5306	50.5898	-0.145633	0.092509	-0.0156627	(Bullister and Weiss 1988)
CFC-113 (C ₂ Cl ₃ F ₃)	-134.243	203.898	54.9583	-0.02632	0.005874	–	(Bu and Warner 1995)
SF ₆	-80.0343	117.232	29.5817	0.0335183	-0.0373942	0.00774862	(Bullister et al. 2002)
SF ₅ CF ₃	-12.8108	23.9976	-3.9715	–	–	–	(Busenberg and Plummer 2008)

dependent on the atmospheric pressure and the solution temperature and salinity. The mole fraction of the gas above the solution is given by the equation:

$$x_i = \frac{m_i}{K_h(P - p_{H_2O})} \quad (2)$$

where x_i is the dry mole fraction of the i th tracer, m_i is the molar concentration, P is the atmospheric pressure, and p_{H_2O} is the vapor pressure of water, respectively. p_{H_2O} is given by the empirical equation:

$$p_{H_2O} = e^{(24.4543 - 67.4509 * (\frac{100}{T}) - 4.8489 \ln(\frac{T}{100}) - 0.000544 * S)} \quad (3)$$

where S is the salinity of the water in per mill and T is the temperature in degrees Kelvin (Weiss and Price 1980). The Clarke-Glew-Weiss equation (Eq. 4) is commonly used to parameterize the temperature- and salinity-dependent gas solubilities (Table 1) (Warner and Weiss 1985; Bu and Warner 1995; Bullister et al. 2002; Busenberg and Plummer 2008):

$$\ln K_h = A + B \times \left(\frac{100}{T}\right) + C \times \ln\left(\frac{T}{100}\right) + S \left(D + E \left(\frac{T}{100}\right) + F \left(\frac{T}{100}\right)^2 \right) \quad (4)$$

where A , B , C , D , E , and F are fit coefficients and T is the equilibrium (recharge) temperature in degrees Kelvin. The solubilities for atmospheric age tracers are shown in Fig. 2.

Historical Atmospheric Concentrations

Ascertaining the historical atmospheric concentrations of tracers is of critical importance to dating with environmental tracers. The historic concentrations of halocarbons have been measured and extensively studied because of their role in atmospheric chemistry and potent radiative forcing properties (IPCC 2007; WMO 2010; Montzka, et al. 2011; Garcia et al. 2012). Many halocarbons that are stable in groundwater systems are routinely measured in a network of ground stations around the world by the National Aeronautics and Space Administration (NASA)-funded Advanced Global Atmospheric Gases Experiment (AGAGE) and the National Oceanic and Atmospheric Administration Earth System Research Laboratory's (NOAA ESRL) Halocarbons and other Atmospheric

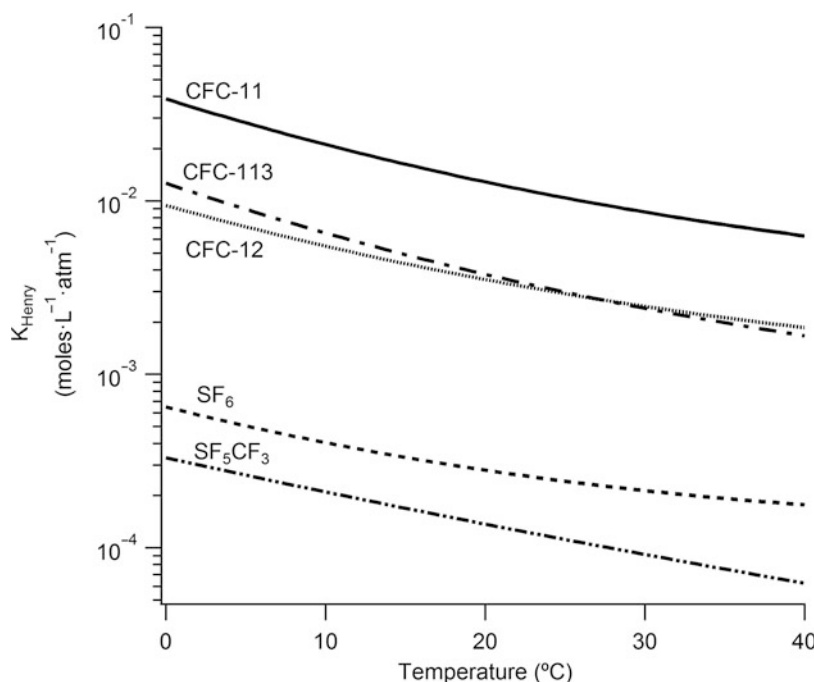


Fig. 2 The temperature-dependent solubility of commonly used environmental tracers in pure water

Trace Species Group (HATS) (AGAGE 2013; HATS 2013). These projects have been collecting archive samples and reporting in situ and flask measurements since 1978. The pre-1976 atmospheric concentrations have been reconstructed from production and release estimates (McCarthy et al. 1977; AFEAS 2013). Measurements are typically reported on calibration scales prepared by NOAA (HATS 2013) or Scripps Oceanographic Institute (AGAGE 2013). The majority of atmospheric tracers are produced and released in the northern hemisphere; consequently, there is an approximate 1-year lag in transport between hemispheres (Seinfeld and Pandis 1998). Local atmospheric sources can increase concentrations above background levels in the vicinity of the source, requiring knowledge of the local history in these instances in order to reliably interpret groundwater ages (Oster et al. 1996; Ho et al. 1998; Cook and Solomon 1997; Cook et al. 2006).

Analytical Methods

Purge-and-trap-based GC-ECD systems are usually used to quantify CFCs, SF₆, and SF₅CF₃ concentrations (Lovelock 1958, 1974; Thompson and Hayes 1979; Bullister and Weiss 1988; Busenberg and Plummer 1992, 2000, 2008; Hofer and Imboden 1998). To quantify the HCFCs, HFCs, and many PFCs, methods employing a GC with mass spectrometer detectors (GC-MS) are used, as these compounds have low response in ECDs (Sousa and Bialkowski 1997; Miller et al. 2008; Deeds 2008; Deeds et al. 2008).

Environmental releases of ultra-trace halocarbons may soon become useful in dating groundwater because of improved sampling procedures in the field. Several techniques are being developed that will allow the extraction of gases from very large volumes of water and enable the use of tracers that have atmospheric concentrations of only a few parts per quadrillion (1×10^{-15}) in dating studies (Johnson 1999; Probst et al. 2007; Loose et al. 2009; Ohta et al. 2009; Busenberg and Plummer 2008; Gardner and Solomon 2009; AGAGE 2013).

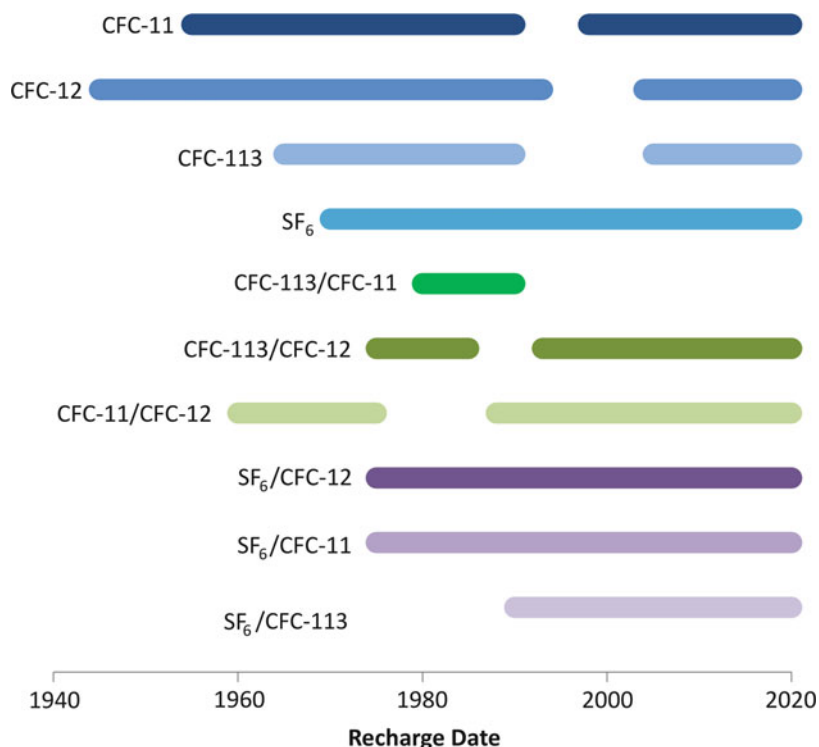


Fig. 3 Useful dating ranges of CFCs, SF₆, and their ratios

CFC-11, CFC-12, CFC-13, and CFC-113

CFC-11, CFC-12, and CFC-113 are commonly used in groundwater dating studies (Thompson and Hayes 1979; Busenberg and Plummer 1992; Ekwurzel et al. 1994; Solomon et al. 1996; Cook and Solomon 1997), as the other CFCs (CFC-114(a), CFC-115, and CFC-13), have low atmospheric concentrations and(or) are more difficult to detect (Busenberg and Plummer 2008). CFC-11 (CCl₃F) and CFC-12 (CCl₂F₂) were extensively used as safe refrigerants, nonflammable aerosol propellants, and blowing agents for foam plastics. Significant production of CFC-113 (C₂Cl₃F₃), a liquid degreaser and cleaning agent, started in the 1950s. CFC-13 (CClF₃) was primarily used as a very low-temperature refrigerant and has shown promise as a dating tool. CFCs are relatively inert with long atmospheric lifetimes (102, 45, and 85 years for CFC-12, CFC-11, and CFC-113, respectively). CFC-11 and, to a lesser degree, CFC-12 and CFC-113 are susceptible to degradation by methanogenic bacteria in aquifers (Lovley and Woodward 1992; Bauer et al. 2001; Sebol et al. 2007; Balsiger et al. 2005; Montzka and Reimann 2010). CFC atmospheric concentrations in the northern hemisphere peaked between 1990 and 2000 (CFC-12 peaked at 546 pptv in 2001, CFC-11 at 272 pptv in 1994, and CFC-113 at 85 pptv in 1996). Atmospheric concentrations are now slowly decreasing with the 2010 northern hemisphere concentrations of 529, 237, and 74 pptv, for CFC-12, CFC-11, and CFC-113, respectively (Montzka and Reimann 2010). This decrease in atmospheric concentrations can complicate piston-flow age interpretation of modern waters since there is not a unique age solution. This difficulty may be overcome by using CFC/CFC or CFC/SF₆ ratios or SF₆ concentration to qualify the apparent piston-flow age (Fig. 3) (Busenberg and Plummer 2000; IAEA 2006).

SF₆ and SF₅CF₃

Sulfur hexafluoride (SF₆) is an inert gas that has the highest known dielectric constant. The production of SF₆ began in the 1940s as part of the war effort; the high electrical insulating properties were crucial in the development of million volt x-ray tubes, radar, and the first atomic bombs (Preston 2003). Large-scale production began in 1953 with the introduction of SF₆-filled electrical switches and transformers (Ko et al. 1993; Maiss and Brenninkmeijer 1998; Busenberg and Plummer 2000). SF₆ has also been used extensively in oceanic tracer studies and as an inert blanketing gas in the melting and production of magnesium metal (Maiss et al. 1996; Wilson and Mackay 1996; Caplow et al. 2003; Hall et al. 2011; Smith et al. 2011). A natural atmospheric steady-state preindustrial background source of <0.05 pptv has been recognized and is thought to originate from silicate-rich igneous rocks, the mineral fluorite (CaF₂), some natural gases, and ancient groundwater (Maiss et al. 1996; Harnisch et al. 2000; Busenberg and Plummer 2000). These geologic sources can cause elevated levels of SF₆ in some aquifers above atmospheric equilibrium and complicate dating (Busenberg and Plummer 2000; Deeds et al. 2008; von Rohden et al. 2010a). SF₆ is an important dating tracer because, unlike CFCs, it is not known to be susceptible to microbial degradation and it has an estimated atmospheric lifetime between 800 and 3,200 years; thus, atmospheric concentrations are not expected to decrease in the foreseeable future (Ko et al. 1993; Levin et al. 2010).

SF₅CF₃ was first reported in the atmosphere by Sturges et al. (2000) and is entirely of anthropogenic origin. SF₅CF₃ does not have commercial applications and is believed to be a by-product of production of some fluorochemicals (Sturges et al. 2000; Santoro 2000; Erboy and Smethie 2012; Sturges et al. 2012). SF₅CF₃ has been used as a dating tool in groundwater studies (Busenberg and Plummer 2008) and as a tracer in hydrologic studies (Sturges et al. 2000; Ho et al. 2008; Busenberg and Plummer 2010). Samples of air from polar snowpack (“fern”) and archived air show that the atmospheric SF₅CF₃ concentration increased from <0.005 pptv in the 1960s to 0.158 pptv in 2008 after which the SF₅CF₃ concentration plateaued due to changes in fluorochemical production methods (Sturges et al. 2000, 2012; Busenberg and Plummer 2008).

Perfluoroalkanes (C_nF_{2n+2}) and Cyclic Perfluorocarbons

The most abundant PFC in the atmosphere is CF₄. Like SF₆, it has both natural and anthropogenic sources, with a preindustrial steady-state atmospheric concentration of 34 ± 1 pptv. After 1960, the concentration increased to the present concentration of ~80 pptv (AGAGE 2013; Simmonds et al. 2002; Mühle et al. 2010). The next most abundant PFC, C₂F₆, had a preindustrial background concentration of <0.3 and the concentration has increased to ~3.5 pptv as of 2010 (Worton et al. 2007; AGAGE 2013). CF₄ occurs naturally in fluorite minerals and granite (Harnisch et al. 1996, 2000) and is also present in significant concentrations in natural gas and in deep groundwater (Deeds 2008). CF₄ and C₂F₆ are produced at the graphite anodes during Al production (Roberts and Ramsey 2013). C₃ to C₈ perfluorocarbons have been detected in the atmosphere and their concentrations are increasing (Mühle et al. 2010; Ivy et al. 2012).

Perfluorocycloalkanes are very stable compounds and are increasing in the atmosphere (Straume et al. 1998; Watson et al. 2007) and have been successfully used to trace air masses and may be used in future groundwater studies (Watson et al. 2007). They cannot be easily analyzed by GC-ECD, and research into detection approaches using specialized GC mass spectrometry

(GC-MS) and negative chemical ionization mass spectroscopy (GC-NCI-MS) is ongoing (Galdiga and Greibrokk 1997; Simmonds et al. 2002; Miller et al. 2008).

Nitrogen Trifluoride

Prather and Hsu (2008) recognized the potent greenhouse gas NF_3 in the atmosphere, which has a lifetime of 740 years (Prather and Hsu 2008). NF_3 is extensively used in the electronics industry for equipment cleaning, for etching of microcircuits, and in the manufacture of flat-panel displays and thin-film photovoltaic cells (Weiss et al. 2008). The NF_3 concentrations have increased from about 0.02 pptv in 1978 at a rate of 11 % per year to 0.45 in 2008 (Weiss et al. 2008) and may have uses in future hydrologic investigations.

Summary

Anthropogenic atmospheric tracers have been extensively used in hydrologic tracer studies and in groundwater dating studies. CFCs and SF_6 were the most extensively used tracers; however, many other environmental tracers (SF_5CF_3 , CFC-13, PFCs, and HFCs) show potential as dating tools pending development of improved analytical methods. Dating of groundwater using the piston-flow model, lumped-parameter mathematical models, or reactive transport flow models requires the knowledge of recharge conditions (recharge temperature and pressure and vadose zone thickness) and aquifer properties that affect the dissolved tracer concentrations in the sample (adsorption, contamination, degradation).

Cross-References

- ▶ Bomb Carbon
- ▶ Noble Gas Mass Spectrometer
- ▶ Water (^{14}C)
- ▶ Relative Dating Methods
- ▶ U-Th:He Dating

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Dendrochronology, Entomology

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Definition

Dendroentomology, a subfield of dendrochronology, documents past occurrence of forest insect outbreaks, and provides an understanding of insect population dynamics, including duration of outbreaks, interval between outbreaks and spread. (Speer 2010)

Dendroentomology is the study of spatiotemporal patterns of herbivory caused by forest insects, based on inferences from (1) the analysis of annually resolved tree-ring data and (2) relatively robust species associations between forest insects and the host-tree tissues that they tend to prefer to consume. See also the definition in Text Box 1.

Introduction

As illustrated in Text Box 1, dendroentomology is related to dendrochronology – which is the use of annually resolved tree rings to date growth anomalies (narrow rings, frost rings, discolored rings, etc.) within woody samples (stems, roots, branches) and to cross-date such anomalies across samples. Dendroentomology is a subfield of dendroecology – which is the use of annually resolved tree rings to accurately date (Stokes and Smiley 1996), and to study, growth anomalies related to ecological factors (including site and species characteristics) that affect tree growth rates. It is distinct from, but not unrelated to, dendroclimatology – which is the use of annually resolved tree rings to date and to study growth anomalies related to climatic events of the past, especially as pertaining to positive and negative anomalies in temperature, precipitation, radiation, etc., which influence tree growth rates (Fritts 1976).

For foliage-grazing insects, such as the defoliating Lepidoptera (caterpillars) or Hymenoptera (sawflies), it is often possible to study negative growth anomalies in extant trees (or coarse woody debris) that are not attributable to climate and to attribute them to a foliage-grazing insect that does not kill its host tree. Because tree growth rings, when properly prepared, are annually resolved, it is often possible to date such impacts with relative accuracy, to the year in which the impact occurred.

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Text Box 1 Definitions from Grissino-Mayer’s (2014) “Principles of Dendrochronology”

Henri Grissino-Mayer (2014) provides a definition of dendrochronology that is broadly inclusive:

Dendrochronology: The science that uses tree rings dated to their exact year of formation to analyze temporal and spatial patterns of processes in the physical and cultural sciences.

such that dendroentomology is considered as one of many subfields of dendrochronology:

Subfields of Dendrochronology

- **Dendroarchaeology:** Dating of Archaeological dwellings.
- **Dendroclimatology:** Developing a record of past climate.
- **Dendrogeomorphology:** Dating land movements such as landslides in the past.
- **Dendrohydrology:** Creating a record of past water availability and flooding.
- **Dendroglaciology:** Dating past movements of glaciers.
- **Dendrovolcanology:** Dating the past eruptions of volcanoes.
- **Dendrochemistry:** Using tree rings as a monitor of the chemical makeup of the soil.
- **Dendroecology:** Recording ecological processes such as tree-line movement, insect outbreaks, or movement of invasive tree species.
- **Dendropyrochronology:** Dating the past occurrence of forest fires.
- **Dendroentomology:** The use of tree rings to reconstruct past population levels of insects.
- **Dendromastecology:** The use of tree rings to reconstruct fruiting events in trees

Table 1 Tree-defoliating insects which have been a target of dendroentomological reconstruction of past outbreaks

Host-tree species	Defoliator insect species	Geographic region	Authority
Douglas fir	Western spruce budworm	USA	Swetnam and Lynch (1993)
Eastern larch	Larch sawfly	Canada	Jardon et al. (1994)
European larch	Larch budmoth	Switzerland	Weber (1997)
Ponderosa pine	Pandora moth	USA	Speer et al. (2001)
Trembling aspen	Forest tent caterpillar	Canada	Cooke and Roland (2007)
White spruce	Eastern spruce budworm	Canada	Boulanger et al. (2012)
Douglas fir	Western spruce budworm	Canada	Alfaro et al. (2014)

Applications

Some well-known examples of applications in dendroentomology are provided in Table 1.

For phloem-feeding, fungus-vectoring bark beetles (Coleoptera: Scolytidae), which tend to kill their hosts in order to successfully reproduce, herbivory is inferred not from negative anomalies in annual radial growth, but positive anomalies among surviving trees that did not experience lethal attack (Campbell et al. 2007).

The attributes of tree rings that are used to infer past entomological disturbances may include radial ring width, the ratio of latewood to earlywood, wood density, chemical profiles, and characteristic mis-colorations associated with altered wood chemistry and/or cell structure.

The reconstruction of herbivory events though time is necessarily an imprecise science, as (1) the association between insect species and tree species is typically not strictly one-to-one, but rather several-to-several, where there are several potential herbivore species that might grow to significant numbers on a given tree species, and (2) insect populations, when they rise, do not always grow to devastating levels, and light herbivory will be indistinguishable from background variations that are expected to result from numerous ancillary agents, especially moisture or temperature limitations occurring during the growing season.

Frequently, the study of neighboring tree species that are typically not defoliated by the target insect species of interest will be studied as a “control.” If this control species is not attacked by either the target insect or other insects and if, further, its responses to climatic fluctuations mirror those of the primary host-tree species that is attacked, then the two species will tend to share a common dendroclimatic signal that may be removed by subtraction, thus enhancing the target signal of interest to the dendroentomologist.

Uncertainty in the reconstruction of entomological history includes imprecision in dating accuracy and imprecision in impact calibration. Dating accuracy within a sample is limited by the fact that radial tree growth responses often lag a year and more behind the herbivory event. Dating accuracy across samples is limited by the fact that while climatic influences may be highly correlated across samples, entomological disturbances may or may not be as highly correlated. For example, a spreading epidemic will result in spatial and temporal lags in growth reductions occurring across samples. This hinders the otherwise straightforward procedure of accurately cross-dating samples by “wiggles matching” the high-frequency variations in ring attributes over time (Stokes and Smiley 1996).

Estimating the proportion of sample trees affected during an insect outbreak is sensitive to assumptions about the relationship between insect population density, defoliation levels, and the impact of defoliation on the ring attributes of interest, and in many cases these assumptions are not verified. Outbreak reconstructions therefore typically carry an unknown level of imprecision. A final, irreducible source of imprecision and bias is the fact that historical reconstructions tend to make use of living samples, which are the survivors of previous disturbance events. As the most intensely attacked trees are selectively removed from the extant population available for sampling, the result is an unstably biased reconstruction signal, with an unknown level of bias that grows over time with each disturbance event that removes trees from the sampling population (Cooke et al. 2003).

When insect populations are extremely high, the mortality that occurs, through the creation of gaps in the forest canopy, gives rise to the establishment of a new cohort of seedlings and saplings. Indeed, the mortality that may occur during heavy defoliation events leads to characteristic patterns of cohort development which may be used to supplement inferences about the impact of past outbreaks.

The reconstruction of past herbivory based on tree rings is aided by, but distinct from, the study of insect paleomacrofossils, which are fossilized remnants of insect body parts (e.g., heavily sclerotized mouthparts, head capsules, or wings) or frass (i.e., excrement), which are often taxonomically unique identifiers to the species level. A thick deposit of macrofossils of a particular insect species that is found in an ancient lake or bog may be carbon-dated (within a limited range of accuracy), thus providing corroborating evidence for inferences drawn from tree-ring analysis (Bhiry and Filion 1996; Simard et al. 2006; Brunelle et al. 2008).

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Luminescence Dating of Shell-Rich Deposits

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Synonyms

OSL of anthropological shell middens; OSL of shell mounds; OSL of geological layers rich in shells

Definition

Shell-Rich Deposits. Any stratum composed primarily of shells which consist of either aragonite or calcite biomineral. The remaining materials maybe a complex composition of siliciclastic or carbonate grains with or without carbonate cement.

Introduction to Shell-Rich Deposits and OSL

Although optically stimulated luminescence dating (OSL) and/or infrared stimulated luminescence dating (IRSL) is typically used in environments where the predominant clasts or grains consist of sand-size particles of quartz and feldspars, shell-rich deposits containing these grains can also be dated using this method. These shell-rich deposits can be either of marine or lacustrine origin, or artificial concentrations created by humans. This allows OSL to be used to answer chronologic questions pertaining to geologic processes and features and well as anthropological sites and events. Many studies traditionally obtain chronologic information from shell deposits using radiocarbon (^{14}C), $^{230}\text{Th}/^{234}\text{U}$, and amino acid racemization.

Geological shell deposits are formed when coastal processes concentrate the shells by either winnowing fines or depositing larger shells within a particular portion of the near-shore zone. Examples of these environments include shell lags created as the result of sea-level transgressions and regressions as well as chenier plains formed from tidal action (Rosendahl et al. 2007; Masselink et al. 2011). Determining the age of these deposits can provide important information about the history of coastal processes in a region.

Anthropological concentrations of shells are generally termed shell middens and are common in coastal environments. Shell middens are best defined by Waselkov (1987) as a human created cultural deposit in which the main material constructing the deposit is shells and shell fragments. This loose definition can include deposits of shells discarded by humans in a haphazard manner (i.e., a trash pile) or shells used for a specific purpose, such as the construction of a building or monument. The age of a shell midden can be used to determine the age of artifacts of cultural significance found within the midden. Shell middens are formed from processes completely

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different from coastal deposits, but differentiating them from natural shell accumulations can be difficult (Rosendahl et al. 2007). For further discussion on the cultural significance and identification of shell middens, readers are referred to Waselkov (1987) and Rosendahl et al. (2007).

While OSL has been used with success in the shallow marine and coastal environments (see Jacobs (2008) for a detailed review), the deposits that are targeted are generally composed of sand. Most studies that endeavor to determine the age of a shell-rich horizon use OSL on sand layers above or below the shell layers (Stone and Cupper 2003; Parker and Goudie 2007; Bateman et al. 2008). However, OSL on quartz sand grains within shell layers has been used with success (Lopez 2007; Thompson et al. 2007; Burdette et al. 2009; Pluckhahn et al. 2014). There has also been a published report of using IRSL to determine the age of feldspar grains from within a shell-rich deposit (Mauz 1999). The dating of sediments with abundant calcite cements commonly referred to “beach rock” (Frechen et al. 2001; Tatum et al. 2003; Frechen et al. 2004) is similar to the dating of shell-rich layers and shares the same challenges with regard to determination of the long-term dose rate.

This article will highlight as a case study in the use of OSL in shell-rich deposits in several anthropological shell middens at the Crystal River Site on the Crystal River in Dixie County, Florida USA. Based on artifactual content and radiocarbon dating, this site experienced human occupation during the Woodland Period from 1000 BC to 1000 AD and includes a number of burial and ceremonial mounds (Thompson and Pluckhahn 2010). The mounds at the Crystal River Site provide an opportunity to compare results of OSL and radiocarbon dating.

Advantages and Disadvantages of Using OSL Relative to Other Geochronologic Methods

The main advantage that OSL has over other methods commonly used to determine the age of shells and shell-rich horizons, such as ^{14}C , ($^{230}\text{Th}/^{234}\text{U}$), and amino acid racemization (AAR), is that it determines the age of a depositional process, not a biological event. This allows for the age of the shell deposit to be determined regardless of the age of the individual shells that compose the deposit. Studies of modern marine shell deposits (Flessa et al. 1993; Wehmiller et al. 1995; Carroll et al. 2003) have shown that the average age of the shells composing these deposits are far from modern. Flessa et al. (1993) discovered that the average shell in their modern study area was approximately 450 years old, with shells over 3.5 ka present. These results are not surprising when considering that these types of deposits represent time-averaged assemblages (Kowalewski 1996). This attribute can prove to be a significant barrier to determining the true age of the depositional process that brought all the shells together. These studies show that any depositional process occurring on a thousand year or smaller time scale might not be resolved by dating of the shells themselves due to the range of shell ages (Flessa et al. 1993).

Radiocarbon

Radiocarbon dating of marine shell requires a carbon reservoir correction in order to account for the age of the inorganic carbon taken up by the shell during growth (see section on [Cross-References](#)). These corrections can be quite large and require information about the conditions where the shell formed. The use of OSL eliminates the uncertainties associated with the estimation of the reservoir effects of a particular location. Studies such as Bateman et al. (2008) have used the combination of

OSL and ^{14}C to highlight the need for further investigation of the reservoir effects of local sites. Dating sand found within a shell deposit can provide independent age control to sites that have had extensive research into the areas local carbon reservoir. Stone and Cupper (2003) also exemplify the usefulness of using OSL when contamination of radiocarbon samples is suspected.

$^{230}\text{Th}/^{234}\text{U}$

The $^{230}\text{Th}/^{234}\text{U}$ dating method uses the ratio of parent (^{234}U)-to-daughter (^{230}Th) isotopes within the uranium decay chain to determine the age of a particular object (see [Cross-References](#)). Mollusks, particularly oyster, are a major component in many shell middens (Waselkov 1987). Unfortunately oysters often exhibit post-burial open-system behavior where parent and daughter isotopes are added or removed through diagenetic processes (Kaufman et al. 1971; Blackwell and Schwarcz 1995; McLaren and Rowe 1996; Edwards et al. 2003; Calsteren and Thomas 2006). This makes oysters difficult to date with U-series. OSL does not rely on isotopic ratios to determine the age of a deposit and can be used on shell deposits that may experience this open-system behavior. However, the open-system behavior can lead to problems with dose-rate determination, because uranium is mobilized through this process.

Amino Acid Racemization (AAR)

AAR dating uses the racemization, or change, of amino acid peptides that occur over time after the death of an organism to determine the time since death (see section on [Cross-References](#)). The rate of the racemization process is dependent on the temperature, pH, and species of the sample. Many of these factors have to be estimated when attempting to determine the age of a sample (Rutter and Blackwell 1995; Wehmiller and Miller 2000; Wehmiller 2012). Due to the many factors associated with the determination of an AAR shell age, this technique often lacks the high resolution needed in many Holocene and Pleistocene geologic and archaeological sites. OSL can provide the independent age confirmation in shell deposits in which one may wish to attempt to use AAR.

Heterogeneity and Uranium Uptake/Loss

OSL requires that the annual radioactive dose rate of the material be known to calculate the age of a sample. In sandy deposits, this is relatively straightforward as sediment is generally homogeneous in composition and radioactive dose within distances that affect the samples. In shell-rich deposits, the larger shells can lead to the formation of heterogeneous radioactive doses to the sample complicating the calculation of the annual dose rate. Furthermore the open-system behavior of oyster shells with respect to uranium can have a significant impact on dose rates through time, leading to larger errors in the age estimation of older shell-rich horizons (Zander et al. 2007; Burdette et al. 2009). While this open-system behavior has been studied (Prescott and Hutton 1995; Olley et al. 1996; Zander et al. 2007), more research specific to OSL dose rates in shell-rich deposits is needed.

Obtaining and Isolating Quartz

There are some specific problems with sample collection and preparation. Unlike sand deposits, the large shells or dense shell concentrations can make it difficult to collect a sample using a sample tube or core. To overcome this problem, a sample taken by hand at night maybe necessary. Samples of a shell-rich deposit may also need to contain more material than a bulk sample from a sand-rich environment so that enough quartz can be collected. After the sample is prepared, it generally yields only a very small amount of pure quartz. Quartz sand will adhere to shells, and a gentle agitation maybe required to separate quartz from the larger shells (brushing the sand off works well). The sieved fraction needs some special care because its high calcium carbonate fraction causes a vigorous reaction at the beginning of the acid dissolution step and may require several repeat dissolutions to isolate the non-carbonate fraction.

Case Study of Crystal River

Crystal River and Roberts Island are neighboring archaeological sites. Of the many mounds present, three mounds were studied. One composed of about 98 % whole oyster shells (Roberts Mound) and two constructed of sand with few shell fragments (Mounds A and H). Radiocarbon dates obtained from Roberts Mound as well as other artifacts at the site provide general age control and make the site an excellent opportunity to use OSL on a shell-rich deposit and compare it to the results of sand-rich deposits (Pluckhahn et al. [2014](#)).

Vertical push-core samples were taken from the sandy Mounds A and H, while a sample collected by hand at night was collected at Roberts Mound. A Harwell gamma spectrometer was used in vertical holes to determine the annual gamma dose rates in Roberts Mound to try to avoid any homogeneity in dose rate that might have been present. Less than about 2 % of the total materials in the mound were sediment, the remainder being air space and oyster shell. In Roberts Mound, the beta dose rate (reconstructed from uranium, thorium, and potassium concentrations) of the sediment and the beta dose rate contributed by the shells were calculated separately. The shell beta dose rate proved clearly more appropriate, as using the sediment itself to calculate this leads to major underestimates of the age based on radiocarbon dating. Moreover, the results of these calculations showed that the shells contributed less than 10 % of the total annual dose compared to the dose sourced from the sediment and cosmic radiation sources (Pluckhahn et al. [2014](#)). It was also found that the oyster shell beta plus gamma dose rate comprised only 50–60 micrograys per year, which was only about 20–25 % of the total dose rate to the quartz grains (the remainder coming from cosmic rays). To a large extent, this ameliorates any affects associated with changing dose rate in the shells due to uranium uptake or loss during open-system behavior at Roberts Mound. However, this is only the case for sites where shell makes up such a large proportion of the buried material.

Results of the OSL analysis of Roberts Mound correlate well with radiocarbon ages from the mound. At the Crystal River site, OSL ages of Mounds A and H showed some significant age inversions, but a minimum age model in other samples yielded agreement with radiocarbon ages. This latter result is best explained by incomplete bleaching of the sand during the construction of Mounds A and H (Pluckhahn et al. [2014](#)), which were ceremonial in nature.

Summary and Conclusions

OSL is not dependent upon dating biological processes, thus having obvious advantages in some cases over radiocarbon, $^{230}\text{Th}/^{234}\text{U}$, and AAR in the dating of shell-rich deposits. It can provide direct determination of a depositional event and enclosing of archaeological materials, eliminating some of the possibilities of age mixing and allowing for better resolution within Holocene deposits. The main challenges of using OSL within shell-rich horizons include open-system behavior affecting dose rates, and in sandy ceremonial mounds, there is a considerable possibility of incomplete zeroing as sand was poured onto the mound surface during construction.

Cross-References

- ▶ [Amino Acid Racemization Dating](#)
- ▶ [Luminescence Dating](#)
- ▶ [Luminescence Dating of Archaeological Sediments](#)
- ▶ [Luminescence, Coastal Sediments](#)
- ▶ [Carbonates, Marine \(\$^{14}\text{C}\$ \)](#)
- ▶ [Carbonates, Marine Carbonates, \(U-Series\)](#)

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Uranium–Lead Dating, Opal

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Synonyms

U–Pb dating of opal; Uranium–lead ages of opaline silica

Definitions

Uranium–lead dating. A geochronological method that uses final decay products in the ^{238}U and ^{235}U radioactive decay chains to determine the length of time required to accumulate present amounts of stable daughter isotopes ^{206}Pb and ^{207}Pb , respectively.

Opaline silica (opal). A hydrated amorphous form of silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) that commonly contains between 6 % and 10 % water by weight. It precipitates from silica-saturated aqueous solutions at relatively low temperature on or near the surface of the Earth.

Mineralogy and U–Th–Pb Geochemistry of Opal

Due to its amorphous nature, opal is categorized as a mineraloid (Jones and Segnit 1971; Smith 1998), unlike other crystalline forms of silica (e.g., quartz, cristobalite, and tridymite) which are classified as minerals. Opal typically occurs near the Earth's surface where it is deposited in the voids from silica-saturated circulating waters at relatively low temperatures. It is most common in volcanic rocks where volcanic glass is a source of water-soluble silica. Opal also forms in hot-spring mounds and may be a major constituent in petrified wood and other fossil organic substances. As a secondary material, it can replace preexisting minerals such as calcite. Evidence for the opaline silica in young deposits on Mars has been reported (Milliken et al. 2008).

Amorphous opal (called opal-A) forms from maturing silica gel and contains nonstructural water ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). Water contents can reach 10 % and tend to decrease with increasing crystallinity. Subsequent crystallographic ordering and transformations, such as opal-A $\rightarrow$ opal-CT (cristobalite–tridymite) $\rightarrow$ chalcedony (microcrystalline quartz), may be caused by changes in thermal conditions and aging of opal (Kano 1983; Thiry and Millot 1987; Herdianita et al. 2000), although chalcedony also may precipitate directly from solutions at relatively low temperatures ($<100^\circ\text{C}$) (Heaney 1993).

Hydrogenic (water-laid) opal precipitated from oxidizing, near-neutral pH groundwater scavenges U and becomes substantially enriched in U relative to Th and Pb, both of which are much less soluble than U^{+6} under these conditions (Langmuir 1978; Bourdon et al. 2003; Gaillardet et al. 2003). Gaillou et al. (2008) report U concentrations in opals from different continents ranging from

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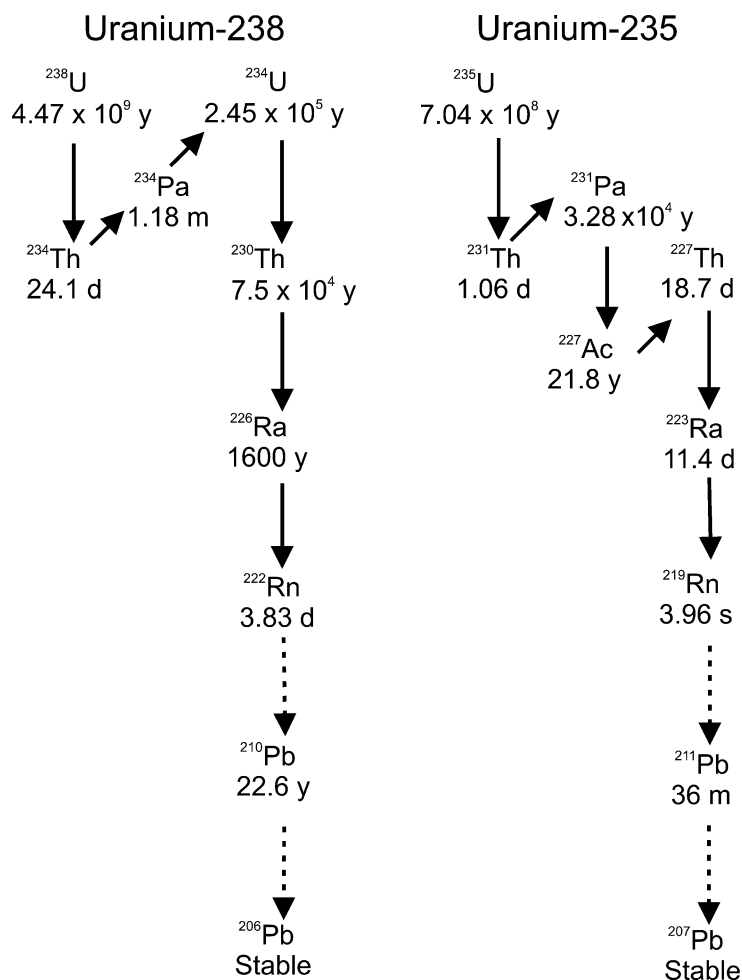


Fig. 1 Simplified ^{238}U and ^{235}U radioactive decay series (Modified from Bourdon et al. 2003)

<0.1 to 131 ppm. Larger U concentrations, up to thousands of ppm, have been reported for common opals from the USA (Ludwig et al. 1980; Neymark and Paces 2000; Neymark et al. 2000; Amelin and Back 2006; Paces et al. 2010). Amelin and Back (2006) observed that most common opal samples they analyzed are enriched in U relative to average upper crust, whereas all other measured elements are depleted. In contrast, precious opals are not enriched in uranium and their crust-normalized U abundances were similar to crust-normalized REE abundances in the same samples. In common opals, measured $^{238}\text{U}/^{204}\text{Pb}$ values range between about 41,000 and 8,700,000, whereas in precious opals these ratios were much lower (1.9–15.2). All of these observations indicate that common opal can be a promising U–Pb geochronometer, whereas precious opals probably are not suitable for U–Pb dating.

Because amorphous opal-A forms from maturing silica gel precipitated from water (Ludwig et al. 1980; Zielinski 1980), its U–Pb age would reflect the time when the redistribution and migration of dissolved ions terminated within the precipitating solid phase. This is probably very close to the time of the silica gel deposition, assuming closed-system behavior from that time until the present. However, subsequent crystallographic ordering and transformations (possibly due to thermal conditions and aging) may complicate the exact meaning of U–Pb ages of opal containing some crystalline silica.

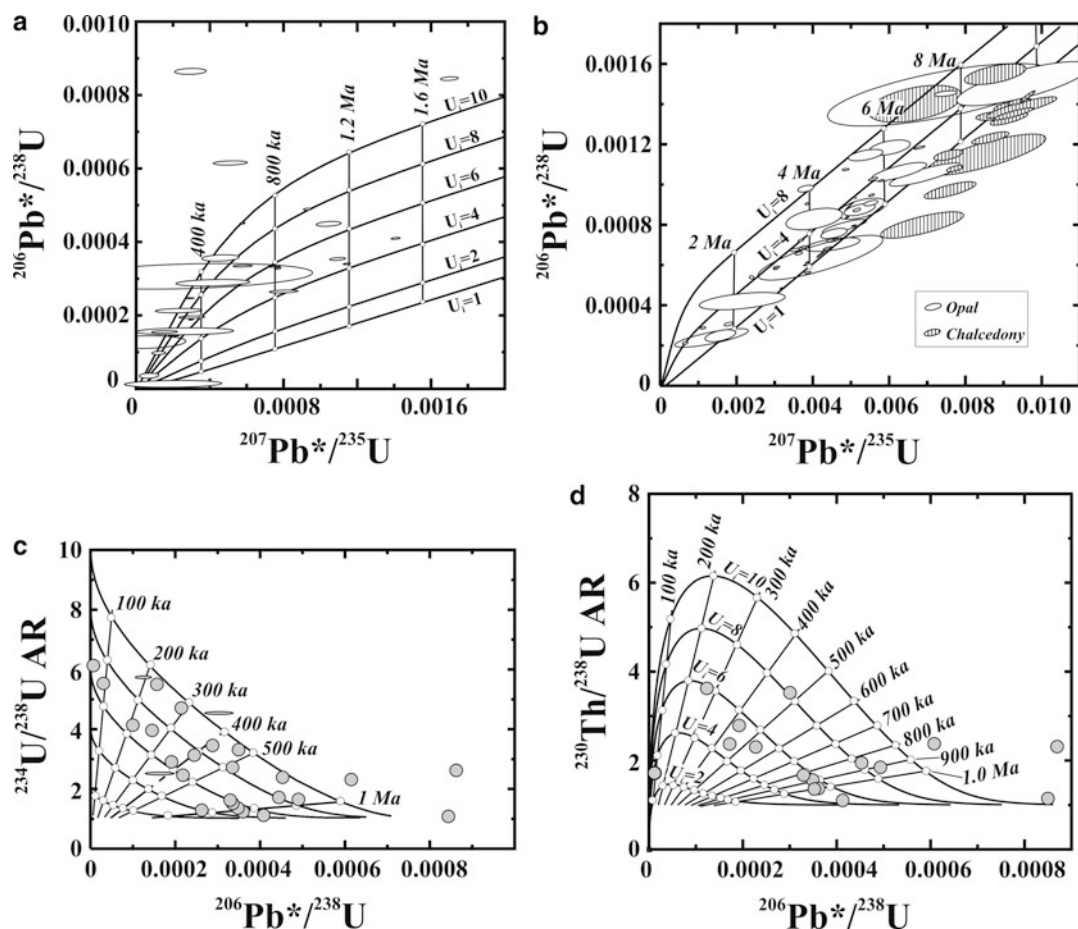


Fig. 2 Concordia diagrams for the case of initial radioactive disequilibrium in U decay chains showing TIMS data for opal from fracture coatings in the vadose zone at Yucca Mountain, Nevada (Modified from Neymark et al. 2000). (a) Common-lead-corrected $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{235}\text{U}$ ratios for opal samples from *outer* portions of the coatings. (b) Opal and chalcedony samples from deeper layers in the coatings. Data in (a) and (b) are plotted with a series of Concordia curves corresponding to different $^{234}\text{U}/^{238}\text{U}$ initial activity ratios (U_i). U–Pb isotope data are shown as 2σ error ellipses. Higher common-lead correction in some samples causes large uncertainties in $^{207}\text{Pb}^*/^{235}\text{U}$ ratios and results in near zero error correlation. The distribution of the data indicates a range of U_i values from ~2 to >10. Isochrons are shown as vertical *dotted lines* connecting points of equal age on the Concordia curves. These isochrons are labeled in thousands or millions of years (ka and Ma, respectively). (c) $^{234}\text{U}/^{238}\text{U}$ AR– $^{206}\text{Pb}^*/^{238}\text{U}$ and (d) $^{230}\text{Th}/^{238}\text{U}$ AR– $^{206}\text{Pb}^*/^{238}\text{U}$ Concordia diagrams for young opal samples showing U-series disequilibrium. U–Pb isotope data are shown as 2σ error ellipses if larger than symbol size. Families of evolution curves corresponding to different U_i values and isochrons connecting points of equal age are shown

The first U–Pb dating of uraniferous opals (from Spor Mountain, Utah; Ludwig et al. 1980) showed that such material is suitable for geochronologic purposes. Subsequent studies (Neymark et al. 2000, 2002; Amelin and Back 2006; Nemchin et al. 2006; Neymark and Paces 2013) have expanded the knowledge base and refined the techniques for interpretation of opal geochronology.

U–Pb Dating of Opal and Initial Radioactive Disequilibrium

Common-Pb-corrected $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{235}\text{U}$ ratios yield two independent apparent ages for the same material based on the two different radioactive parent isotopes (Faure 1986).

Concordance of ages between these two systems is an important check for closed-system behavior with regard to gains or losses of uranium and its daughter nuclides. The conventional method of calculating U–Pb isotope ages assumes that all intermediate daughter isotopes in ^{238}U and ^{235}U decay chains (Fig. 1) were in secular equilibrium at the time of opal formation (i.e., radioactivity of all daughter isotopes was equal to that of the parent). This condition is not fully accomplished for most natural systems because of differences in geochemical behavior of parent and daughter elements (e.g., U, Th, Pa, Ac, and Ra). For example, ^{234}U (intermediate daughter isotope of ^{238}U , Fig. 1) enters solutions preferentially during water–rock interaction due to several decay-related mechanisms such as direct α -recoil of its short-lived parent ^{234}Th (Kigoshi 1971), leaching from damaged sites in crystalline lattice (Szilard–Chalmers effect), and increased aqueous mobility due to radiation-induced oxidation of ^{234}U to the +6 valent state (Gascoyne 1992). As a result, natural waters typically are ^{234}U -enriched with $^{234}\text{U}/^{238}\text{U}$ activity ratio (AR) > 1 (Porcelli 2008 and references therein). Hydrogenic opal inherits this ^{234}U enrichment, which causes its conventional $^{206}\text{Pb}^*/^{238}\text{U}$ ages to be biased to older values. This bias is partially compensated by the initial deficit of ^{230}Th (daughter isotope of ^{234}U , Fig. 1), which is not mobile in groundwater. For example, if an opal sample has a measured $^{206}\text{Pb}^*/^{238}\text{U}$ value of 0.0002, its conventional $^{206}\text{Pb}^*/^{238}\text{U}$ equilibrium age is 1.29 Ma, but in a case of no initial ^{230}Th , its true age will be 1.40 Ma, causing an age bias of –0.11 Ma. The age bias for the same sample is about –0.09 Ma if the initial $^{234}\text{U}/^{238}\text{U}$ AR = 1.6, but the effect of larger ^{234}U excess is much more significant and reaches +0.8 Ma for initial $^{234}\text{U}/^{238}\text{U}$ AR = 5.0. Similarly, conventional $^{207}\text{Pb}^*/^{235}\text{U}$ ages of opal may be biased to younger values due to initial deficit of ^{231}Pa (intermediate daughter isotope of ^{235}U , Fig. 1), which is also poorly soluble in groundwater. The maximum bias in opal $^{207}\text{Pb}^*/^{235}\text{U}$ age is –0.046 Ma in the case of zero initial ^{231}Pa .

In order to calculate U–Pb opal ages, it is necessary to use more general forms of age equations that take into account initial radioactive disequilibria of the uranium daughters (Bateman 1910; Ludwig 1977; Catchen 1984; Wendt and Carl 1985; Neymark et al. 2000) instead of conventional U–Pb age equations (Faure 1986).

Neymark et al. (2000) introduced two new Concordia plots ($^{234}\text{U}/^{238}\text{U}$ AR vs $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ AR vs $^{206}\text{Pb}^*/^{238}\text{U}$) (Fig. 2c, d), which are applicable to young opals (<2 Ma) with measured ^{234}U and ^{230}Th disequilibrium. The combination of the U–Pb and U-series geochronometers provides new opportunities for dating young opals as long as the condition of severe initial radioactive disequilibrium is addressed. The use of the combined ^{238}U – ^{234}U – ^{230}Th – ^{206}Pb technique to date Quaternary opals significantly extends the age range beyond that of the $^{230}\text{Th}/\text{U}$ dating method from <500 ka to >1.5 Ma.

U–Pb Dating of Vadose Zone Hyalitic Opal by TIMS

The need to understand the history of water movement through the unsaturated (vadose) zone at Yucca Mountain, Nevada, considered as a possible repository for high-level nuclear waste, prompted substantial dating efforts of secondary opals in fractures and lithophysal cavities within Tertiary tuffs. This opal preserves a record of paleohydrologic conditions at this site; the U–Th–Pb isotopic systems within opal were studied using thermal ionization mass spectrometry (TIMS) in submillimeter-thick outermost layers (Neymark et al. 2000) and in deeper layers of opal and chalcedony (Neymark et al. 2002) from individual mm- to cm-thick calcite and silica coatings. These samples were collected at depths from ~0 to ~350 m below Earth's surface from the walls of an 8 km long and 7.6 m diameter tunnel, excavated beneath Yucca Mountain to the level of the

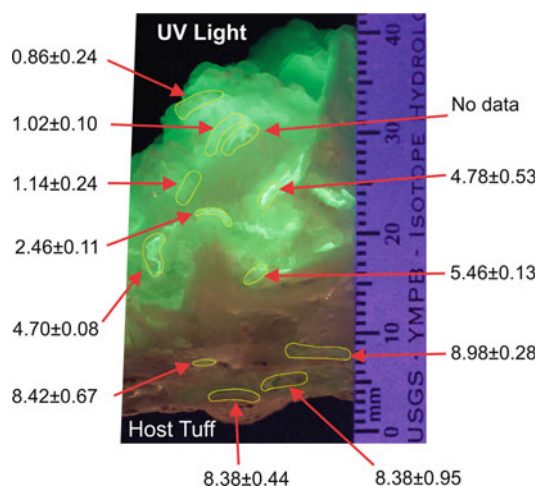


Fig. 3 Locations of opal (green) and chalcedony (brown) subsamples from a mineral coating (sample HD2019, Yucca Mountain, Nevada). TIMS $^{207}\text{Pb}^*/^{235}\text{U}$ ages with 2σ errors in Ma (Modified from Neymark et al. 2003). Opal glows bright green under the short-wavelength UV illumination due to its elevated uranium content

possible repository. The U–Pb ages of the youngest opal from the outermost surfaces of the coatings displayed strong reverse discordance ($^{206}\text{Pb}^*/^{238}\text{U}$ age $>$ $^{207}\text{Pb}^*/^{235}\text{U}$ age, Fig. 2a) because of excess radiogenic $^{206}\text{Pb}^*$ derived from the elevated initial ^{234}U . The data were best interpreted using Concordia diagrams defined by $^{206}\text{Pb}^*/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ AR, and $^{230}\text{Th}/^{238}\text{U}$ AR (Fig. 2c, d). Ages and initial $^{234}\text{U}/^{238}\text{U}$ AR calculated using different Concordias are discordant, that is, observed $^{207}\text{Pb}^*/^{235}\text{U}$ ages of 170–1,772 ka were systematically older than $^{230}\text{Th}/\text{U}$ ages of 34.1–452 ka. In these cases, the age discordance was not interpreted as a result of initial disequilibrium or as mobility of uranium and its decay products under the open system conditions, but rather as a consequence of non-instantaneous growth of opal. Combined U–Pb and $^{230}\text{Th}/\text{U}$ ages support the model of slow mineral deposition (Neymark and Paces 2000) at the rates of millimeters per million years, resulting in layering on a scale too fine for mechanical sampling. In this case, U–Pb ages provided more accurate estimates of the average age for mixed multiage samples than $^{230}\text{Th}/\text{U}$ ages, because ages based on shorter-lived isotopes are nonlinearly biased by younger mineral additions (Neymark et al. 2000).

Uranium and Pb isotopes were also analyzed in deeper layers of opal and chalcedony from individual mm- to cm-thick calcite and silica coatings at Yucca Mountain (Neymark et al. 2002). These opal and chalcedony samples had high U (10–780 ppm) and low common Pb indicated by their large $^{206}\text{Pb}/^{204}\text{Pb}$ values, thus making them suitable for U–Pb age determinations. Similar to U–Pb ages of surface coatings, reverse discordance was also observed for opals from deeper layers within the coatings (Fig. 2b). This opal is sufficiently old to allow nearly all of its initial excess ^{234}U to decay, thus making it difficult to correct for potential bias in $^{206}\text{Pb}^*/^{238}\text{U}$ ages. However, because the $^{207}\text{Pb}^*/^{235}\text{U}$ ages, between 0.6 and 9.8 Ma, are much less affected by the deviation from initial secular equilibrium, they were interpreted as more reliable ages of most silica deposits. Some chalcedony subsamples showed normal age discordance ($^{206}\text{Pb}^*/^{238}\text{U}$ age $<$ $^{207}\text{Pb}^*/^{235}\text{U}$ age, Fig. 2b), so that these ages may represent minimum times of chalcedony formation. Typically, $^{207}\text{Pb}^*/^{235}\text{U}$ ages are consistent with the microstratigraphy of the coatings (Fig. 3), such that the ages increase with increasing depth of the samples. ^{234}U and ^{230}Th in most silica layers deeper in the coatings are in secular equilibrium with ^{238}U (Neymark et al. 2002, 2003), which is consistent with their old age and closed-system behavior during the past ~ 0.5 Ma.

Neymark and Amelin (2008) reported a range of Yucca Mountain opal/chalcedony $^{207}\text{Pb}^*/^{235}\text{U}$ ages from 132.9 ± 8.0 ka to 9.10 ± 0.21 Ma. The ages increased with microstratigraphic depth within coatings and defined slow long-term average growth rates of about 1.2–2 mm/Ma, in good agreement with previous results. These authors concluded that the presence of intermediate daughter isotopes did not appreciably impact the $^{207}\text{Pb}^*/^{235}\text{U}$ ages of opal/chalcedony, which were interpreted as mineral formation ages.

The $^{207}\text{Pb}^*/^{235}\text{U}$ ages of opal and chalcedony intercalated with low-U calcite containing two-phase fluid inclusions were used to constrain timing of fluids with elevated temperatures in the vadose zone at Yucca Mountain (Neymark et al. 2001; Wilson et al. 2003; Whelan et al. 2008). Most $^{207}\text{Pb}^*/^{235}\text{U}$ ages of opal/chalcedony from layers above the calcite that formed at temperatures >30 °C are older than 6–8 Ma. Whelan et al. (2008) interpreted combined opal/chalcedony U–Pb dating and calcite fluid inclusion data as evidence of slow cooling of ~ 13 Ma tuffs within the vadose zone. Wilson et al. (2003) concluded that the results of integrated U–Pb dating of opal/chalcedony and fluid inclusion microthermometry indicate that two-phase fluid inclusion assemblages that trapped fluids of >50 °C are older than ~ 6.3 Ma. Two-phase inclusions in paragenetically later calcite, which formed from fluids of 35–45 °C, are older than ~ 5.3 Ma, and there is no evidence for trapping of fluids with elevated temperatures during the past 5.3 Ma. These data indicate that fluids with elevated temperatures have not been present in the vadose zone at Yucca Mountain since 6–8 Ma.

U–Pb Dating of Opal by SIMS

Several studies (Paces et al. 2001, 2004, 2010) have shown that opal may be finely laminated with growth bands having variable U concentrations and ages. This heterogeneity reflects the time sequence of silica deposition in slow-growing opal and requires high spatial resolution of sampling to minimize the effects of analyzing mixed samples from multiple growth bands (Neymark and Paces 2000; Paces et al. 2001). These studies used TIMS analyses of U, Th, and Pb chemically separated from opal samples of a few to tens of milligrams. Neymark et al. (2000) noted that the relatively large samples used in TIMS-based studies may contain multiple growth zones, producing mixed ages. These ages showed a consistently discordant pattern between $^{230}\text{Th}/^{238}\text{U}$ ages, $^{234}\text{U}/^{238}\text{U}$ model ages, and $^{207}\text{Pb}^*/^{235}\text{U}$ ages and thus required high spatial resolution of sampling. This high sampling resolution can be achieved by in situ dating of opal using the secondary ion mass spectrometry (SIMS), which allows dating of 30- μm -diameter spots on polished opal cross sections.

In situ U–Pb analysis of opal by SIMS or by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) requires a reference opal that has been well characterized by TIMS. This opal must have limited variations in U concentration, low common-Pb abundance, and concordant U–Pb ages to be used as a matrix-matching standard. Amelin and Back (2006) reported structural, geochemical, and TIMS U–Th–Pb and U-series isotopic data for eight samples of precious and common opal, which they tested as potential standards for ion microprobe and LA-ICP-MS isotopic studies. Nemchin et al. (2006) reported the first U–Pb analyses of colorless uraniferous opal from Yucca Mountain, Nevada; Hosszu Hill, Hungary; and Guanajuato, Mexico, using sensitive high-resolution ion microprobe (SHRIMP II). These authors used one of the opals from Amelin and Back (2006) study (sample M21277 from Virgin Valley, Nevada) as a standard and demonstrated the potential of this technique for dating of opal with ages ranging from several tens of thousands years to millions of years. In addition to the high spatial resolution of SHRIMP

analysis, other advantages of the SIMS technique are the following: (1) the ability to analyze in situ all isotopes required to determine both U–Pb and U-series ages, (2) a relatively short analysis time which allows determining the history of opal growth during a single SHRIMP session, and (3) the relatively nondestructive analysis which enables subsequent imaging of the dated samples to aid in interpretation. Nemchin et al. (2013) also emphasized the role of in situ SIMS opal analysis in establishing growth rates of this slowly forming material.

U–Pb Dating of Authigenic and Detrital Opal

The use of the TIMS and SIMS U–Pb dating to establish the age of Neogene–Quaternary clastic sediments was tested on samples of authigenic (formed in situ) and detrital (derived from weathering of the source rocks) opal and chalcedony from boreholes at Midway Valley, Nevada (Neymark and Paces 2013). Dating of authigenic opal that occurs as rinds on rock clasts and in calcite/silica cements establishes minimum ages of alluvium deposition; dating of detrital opal or chalcedony gives the maximum age of sediment deposition.

Large U concentrations (tens to hundreds of ppm) and high U/Pb allowed calculation of $^{206}\text{Pb}^*/^{238}\text{U}$ ages that ranged from 1.64 to 6.16 Ma for authigenic opal and from 8.34 to 11.2 Ma for detrital opal/chalcedony. Samples with the most radiogenic Pb allowed calculation of $^{207}\text{Pb}^*/^{235}\text{U}$ ages, which were concordant with $^{206}\text{Pb}^*/^{238}\text{U}$ ages from the same samples. These ages resulted in the determination of constraints for the timing of the basin development, the rate of erosion of Yucca Mountain, and the last movement on buried faults (Neymark and Paces 2013).

Conclusions

Opal is a hydrogenic mineraloid typically precipitated from silica-saturated solutions near the Earth's surface. Common opal deposited from low-temperature oxidizing groundwater may contain high U concentrations with little or no initial ^{206}Pb and ^{207}Pb , making it a promising candidate for U–Pb dating method. Opal can retain U decay products for long periods of time (>1 Ma) even after some crystallographic ordering and transformation. Samples of slow-growing opal may contain multiage growth zones, thus requiring the use of high spatial resolution in situ analyses for dating. Initial radioactive disequilibrium (^{234}U excess and ^{230}Th deficit) can complicate interpretations of ^{238}U – ^{206}Pb dating results but can be taken into account by combining U-series and U–Pb methodologies for opal samples younger than ~2 Ma. The ^{235}U – ^{207}Pb decay scheme gives more accurate age estimates for older opal samples.

Cross-References

- [Mass Spectrometry](#)
- [Secondary Ion Mass Spectrometry \(SIMS\)](#)
- [Thermal Ionization Mass Spectrometry \(TIMS\)](#)
- [Uranium-Lead Dating](#)
- [Uranium Series, Opal](#)

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Radioactive Decay Constants: A Review

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Definition

The radioactive decay constant (λ) is a characteristic of unstable radionuclides (see chart of the nuclides) that spontaneously decay at different rates to a more stable atomic configuration; the larger the decay constant, the more rapidly the parent radionuclide is depleted with time. The basic formulation of the radioactive decay equation is based on the principle that the number of decay events of any radioactive parent atom is proportional to the number of these atoms present at any given time (Rutherford and Soddy 1902). This basic principle has been transformed into the law of radioactive decay $N = N_0 e^{-\lambda t}$, which states that given an initial number N_0 of radioactive parent nuclei at start time $t = 0$, the number of radioactive nuclei remaining at time t is given by N . Related to the decay constant is the half-life $t_{1/2}$ of a radioactive nucleus: $t_{1/2} = \ln 2/\lambda$. The half-life is the time in which half the number of parent nuclides have decayed.

Introduction

The determination of decay constants and/or corresponding half-lives of radionuclides is a fundamental aspect of geochronologic methods. A wide range of scientific questions can be addressed with dating techniques. A variety of questions can be addressed using dating methods. These range from the age of archaeological materials and human fossils to the age of the oldest materials in our solar system and many geological processes on earth.

The process of radioactive decay proceeds through two main mechanisms: (1) α -decay, which is alpha particle emission (two protons plus two neutrons) from the nucleus, and (2) β -decay, when a nucleus emits an electron or positron. The accuracy and precision of the decay constant measurements are a determinant in the accuracy and precision of the age result. Progress in this area for long-lived radioactive nuclides in part depends on the difficulty in directly measuring the decay events and the range in mass and energy of the different particles emitted during decay. As better methods become available to determine the decay constants for the various methods, more accurate and precise values become available.

Approaches to Determining Decay Constants

There are essentially three different approaches used to determine the decay constant of long-lived radionuclides: (1) direct counting techniques, (2) age comparison of geological materials using multiple dating techniques, and (3) the in-growth method. The direct counting technique involves directly measuring the alpha, beta, or gamma activity, commonly using liquid scintillation counting

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Table 1 Summary of ^{87}Rb decay constant determinations

Reference	Year	$T_{1/2}(10^{10} \text{ a})$	$\lambda (10^{-11} \text{ a}^{-1})$
Age comparisons			
Aldrich et al.	1956	5.0 ± 0.2	1.39 ± 0.06
Steiger and Jäger	1977	4.88 ± 0.03	1.420 ± 0.010
Minster et al.	1982	4.94 ± 0.03	1.402 ± 0.008
Shih et al.	1985	4.94 ± 0.04	1.402 ± 0.011
Amelin and Zaitsev	2002		1.396 ± 0.006
Nebel et al.	2011		1.393 ± 0.004
Absolute counting experiments			
Flynn and Glendenin	1959	4.70 ± 0.10	1.475 ± 0.031
Neumann and Huster	1976	4.88 ± 0.06	1.420 ± 0.030
Kossert	2003	4.967 ± 0.032	1.396 ± 0.009
Ingrowth experiments			
McMullen et al.	1966	4.72 ± 0.04	1.468 ± 0.012
Davis et al.	1977	4.89 ± 0.04	1.419 ± 0.012
Rotenberg et al.	2012	4.9624 ± 0.0065	1.3968 ± 0.0017

Modified after Begemann et al. (2001)

for beta emitters, and dividing by the total number of radiogenic atoms present (e.g., Neumann and Huster 1976; Kossert 2003). The age comparison approach involves selecting relatively simple geological materials and determining their age using multiple dating techniques where the decay constant for the parent isotope in one dating system (e.g., ^{238}U) is considered to be well established and accurate (e.g., Amelin and Zaitsev 2002). The in-growth method involves storing a quantity of purified radioactive parent in a closed container, and after a period of time (typically years to decades), the quantity of daughter isotope is determined using isotope dilution (e.g., Rotenberg et al. 2012).

Tabulations

The strengths and weaknesses of each approach to determinations of decay constants or half-lives are nicely summarized by Begemann et al. (2001), and the range of decay constant values obtained for ^{87}Rb using all three methods are summarized in Table 1. An important aspect of these decay constant determinations is that with improved detection systems and more robust in-growth experiments, there is convergence and general agreement between all three methods for the value of the ^{87}Rb decay constant.

Here, we report on the most recent determinations of the values relevant to geochronology (Table 2). The values are given as either the decay constant with uncertainty or the half-life with uncertainty. The published reported value is shown in bold; the other is calculated from it. Emphasis here was given to reporting not only the values but the research works that actually made the most recent determinations alongside those which have remained in current use for long periods of time. All of the values reported in the tables are revisions of earlier determinations with the exception of Libby 1952. We note that more than half of the values in the table have been reported since 2000. Table 2 is for reference and not meant as a tabulation of “recommended values” for use. Rather, we aim to provide the most up-to-date compilation of the values and let geochronologists themselves decide if the revised values are to become routinely used in practice.

Table 2 Radioactive decay constants and half-lives for selected radionuclides in current use in geochronology

Nuclide	Daughter	Decay constant (a^{-1})	Half-life (a)	Reference	Note
Cosmogenic					
^{10}Be	^{10}B	$(4.997 \pm 0.043) \times 10^{-07}$	$(1.387 \pm 0.012) \times 10^6$	Korschinek et al. 2010	
^{14}N	^{14}C	$(1.2448 \pm 0.0067) \times 10^{-04}$	5568 ± 30	Libby 1952	a
		$(1.2097 \pm 0.0084) \times 10^{-04}$	5730 ± 40	Godwin 1962	b
$^{26}\text{Al}^*$	^{26}Mg	$(9.832 \pm 0.335) \times 10^{-07}$	$(7.05 \pm 0.24) \times 10^5$	Norris et al. 1983 Nishiizumi 2004	
^{40}Ar	^{32}Si	$(4.813 \pm 0.368) \times 10^{-03}$	144 ± 11	Fifield and Morgenstern 2009	
^{40}Ar	^{36}Cl	$(2.3028 \pm 0.0153) \times 10^{-06}$	$(3.01 \pm 0.02) \times 10^5$	NNDC 2012	c
Naturally occurring					
^{40}K	^{40}Ar	$(5.757 \pm 0.016) \times 10^{-11} (\lambda_{\epsilon})$	$(1.2040 \pm 0.0034) \times 10^{10}$	Renne et al. 2011	
^{40}K	^{40}Ca	$(4.955 \pm 0.013) \times 10^{-10} (\lambda_{\beta})$	$(1.3989 \pm 0.0037) \times 10^{09}$	Renne et al. 2011	
^{87}Rb	^{87}Sr	$(1.3968 \pm 0.0027 / -0.0018) \times 10^{-11}$	$(4.9624 \pm 0.0065) \times 10^{10}$	Rotenberg et al. 2012	
^{147}Sm	^{143}Nd	$(6.478 \pm 0.054) \times 10^{-12}$	$(1.070 \pm 0.009) \times 10^{11}$	Kossert et al. 2009	
^{176}Lu	^{176}Hf	$(1.904 \pm 0.018) \times 10^{-11}$	$(3.640 \pm 0.035) \times 10^{10}$	Kossert et al. 2013	d
^{187}Re	^{187}Os	$(1.6668 \pm 0.0034) \times 10^{-11}$	$(4.1586 \pm 0.0085) \times 10^{10}$	Selby et al. 2007	
^{190}Pt	^{186}Os	$(1.414 \pm 0.012) \times 10^{-12}$	$(4.90 \pm 0.04) \times 10^{11}$	Cook et al. 2004	e
		$(1.78 \pm 0.14) \times 10^{-12}$	$(3.9 \pm 0.3) \times 10^{11}$	Tavares et al. 2006	
^{232}Th	^{208}Pb	$(4.948 \pm 0.028) \times 10^{-11}$	$(1.401 \pm 0.008) \times 10^{10}$	LeRoux and Glendinin 1963	f
^{235}U	^{207}Pb	$(0.98485 \pm 0.00067) \times 10^{-9}$	$(7.0381 \pm 0.0048) \times 10^8$	Jaffey et al. 1971	g
		$(0.98571 \pm 0.00012) \times 10^{-9}$	$(7.03196 \pm 0.00086) \times 10^8$	Mattinson 2010	
^{238}U	^{206}Pb	$(1.55125 \pm 0.00083) \times 10^{-10}$	$(4.4683 \pm 0.0024) \times 10^9$	Jaffey et al. 1971	f
^{238}U		$(8.453 \pm 0.103) \times 10^{-17}$	$(8.2 \pm 0.1) \times 10^{15}$	Holden and Hoffman 2000	h
U-series					
^{210}Pb	^{210}Bi	$(3.122 \pm 0.031) \times 10^{-02}$	22.20 ± 0.22	Audi et al. 2003	
^{230}Th	^{226}Ra	$(9.170 \pm 0.013) \times 10^{-06}$	$(75.584 \pm 0.110) \times 10^3$	Cheng et al. 2013	
^{231}Pa	^{227}Ac	$(2.116 \pm 0.007) \times 10^{-05}$	$(32.760 \pm 0.110) \times 10^3$	Robert et al. 1969	
^{234}U	^{230}Th	$(2.822 \pm 0.003) \times 10^{-06}$	$(245.620 \pm 0.260) \times 10^3$	Cheng et al. 2013	
Extinct (i)					
^{244}Pu	Fission	$(1.050 \pm 0.032) \times 10^{-11}$	$(6.6 \pm 0.2) \times 10^{10}$	Holden and Hoffman 2000	h
^{146}Sm	^{142}Nd	$(1.019 \pm 0.105) \times 10^{-8}$	$(68 \pm 7) \times 10^6$	Kinoshita et al. 2012	
		$(6.75 \pm 0.32) \times 10^{-9}$	$(102.6 \pm 4.8) \times 10^6$	Friedman et al. 1966	
^{182}Hf	^{182}W	$(7.788 \pm 0.087) \times 10^{-8}$	$(8.9 \pm 0.1) \times 10^6$	Vockenhuber et al. 2004	

(continued)

Table 2 (continued)

Nuclide	Daughter	Decay constant (a^{-1})	Half-life (a)	Reference	Note
^{41}Ca	^{41}K		$(0.102 \pm 0.007) \times 10^6$	Audi et al. 2003	
		$(6.3 \pm 1.7) \times 10^{-6}$	$(0.11 \pm 0.03) \times 10^6$	Brown et al. 1953	
^{60}Fe	^{60}Ni	$(2.64 \pm 0.04) \times 10^{-7}$	$(2.62 \pm 0.04) \times 10^6$	Rugel et al. 2009	
^{53}Mn	^{53}Cr	$(1.87 \pm 0.20) \times 10^{-7}$	$(3.7 \pm 0.4) \times 10^6$	Honda and Imamura 1971	

General: Bold values are the values reported in the indicated publications. The non-bold value was calculated from it, and its error was calculated using the percentage error of the published value

*Extinct nuclide

^aKnown as the “Libby half-life,” though less accurate, it is still used in conventional radiocarbon dating to calculate conventional radiocarbon years before present

^bThe refined value resulting from three later independent measurements and agreed in conference as the most probable value

^cNational Nuclear Data Center Chart of the Nuclides

^dSee reference for discussion on the “ λ ^{176}Lu dilemma”

^eDue to wide variance in recent determinations, two recent values are given

^fValue accepted by the IUGS-SOG, Steiger and Jäger 1977

^gValue reported here is relative to the widely accepted $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88. A recent study by Hiess et al. (2012) indicates a more accurate estimate of the $^{238}\text{U}/^{235}\text{U}$ ratio in terrestrial samples is 137.818 ± 0.045 (2 σ)

^hSpontaneous fission decay mode

ⁱA more complete list of extinct radionuclides used in meteorite research is reported by Dauphas and Chaussidon (2011)

Cross-References

► [Radiation and Radioactivity](#)

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Volcanic Rocks (K–Ar and Ar–Ar)

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Keywords

K/Ar dating; $^{40}\text{Ar}/^{39}\text{Ar}$ dating; East Africa; Hadar; Hominins; Omo-Turkana Basin

The K/Ar dating scheme, using the conventional K/Ar method, and the closely related $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique, especially the latter, yield numerical ages on igneous rocks that are commonly precise to 1 % or better in the range 0.1 Ma or younger to much older ages (Lee 2014). The younger limit is dependent on detecting radiogenic argon above an atmospheric argon component mainly from the sample itself. The basis for these techniques is described by McDougall (2014) and Lee (2014). The means by which fossils in sedimentary sequences are assigned numerical ages by interpolation between dated volcanically derived beds is illustrated by an example from the hominin-bearing sequence in the Turkana area of East Africa.

Historically, the K/Ar dating method has been of importance in providing age information related to a variety of studies over at least the last five decades, including the delineation and calibration of the geomagnetic polarity time scale, one of the essential foundations for the development of plate tectonic concepts (see McDougall 2013); the numerical calibration of the relative geological time scale, as well as calibration of the evolution of flora and fauna; and the determination of rates of geological processes and the age of individual geological events.

In the $^{40}\text{Ar}/^{39}\text{Ar}$ dating technique, it is the $^{40}\text{Ar}^*/^{39}\text{Ar}_\text{K}$ ratio that needs to be determined (see Lee 2014), and this is derived from the Ar isotopic ratios measured on the argon gas extracted from the sample after irradiation. The equation is listed in McDougall and Harrison (1999, p. 91). McDougall (2014) advocated that the more precise atmospheric argon $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of 298.56 ± 0.31 , given by Lee et al. (2006), be used instead of the recommended Steiger and Jäger (1977) value, derived from Nier (1950), of 295.5, although it makes little practical difference to most calculated ages. It needs to be noted, however, that the latter only applies if all calibrations are done using this newer rather precise value.

The Omo-Turkana Basin Sequence

This stratigraphic sequence, up to 800 m thick, in subaerial exposure, is of significance mainly because of the large number of hominin fossils (>400) that have been recovered over the last five decades by the Leakeys (Leakey and Leakey 1978; Leakey et al. 1998; Feibel et al. 1989; Wood 1991), providing a remarkable picture of the complexity of evolution of hominins. Specimens assigned to *Australopithecus anamensis*, *A. aethiopicus*, *A. africanus*, *A. boisei*, *Kenyanthropus platyops*, *Homo habilis*, *H. rudolfensis*, *H. erectus*, and *H. sapiens* have been recorded (Wood 1991;

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McDougall et al. 2012, etc.). Many other vertebrate fossils have been collected and described from which much information on evolution of genera has been obtained (Harris 1983).

The Omo-Turkana Basin in northern Kenya and southern Ethiopia comprises the depositional environment around the present-day closed basin of Lake Turkana (Fig. 1). Much of the sedimentary material deposited in the basin was brought in by the Omo River, which drains part of the Ethiopian highlands. The basin extends at least 350 km N-S and up to 90 km E-W (Fig. 1) and lies within the East African Rift system where the NNE-SSW trending Ethiopian Rift intersects the N-S trending Kenya Rift. Initially it was thought that the various regions mapped comprised separate depocenters, which is reflected in the stratigraphic nomenclature.

The detrital sediments themselves are not particularly useful for correlation as there are major facies variations from fluvial to deltaic and lacustrine deposits over short distances. Tephra or tuffaceous sediments, usually named as tuffs, with their distinctive elemental signatures of the contained volcanic glass, however, have been the key to stratigraphical correlations from area to area. Chemical analysis of glass shards in these tuffs has shown that some are widespread (Brown et al. 2006), and it has become increasingly obvious that the sediments of the Omo-Turkana Basin are all part of a single depositional system. Some tuffs locally contain pumice clasts, which usually have glass of the same composition as the enclosing tuff, indicating derivation from the same volcanic eruption. The pumice clasts commonly have alkali feldspar (anorthoclase) phenocrysts, which are ideal for isotopic dating by the K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods. The tuffs have facilitated correlations throughout the basin, and some have been isotopically dated, from which a numerical time framework has been developed. Over the last several decades, more than 35 units in the Omo-Turkana Basin have been dated, with most now having been measured using single-crystal $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion techniques (McDougall and Brown 2006, 2008; McDougall et al. 2012). Virtually all these ages are consistent with the stratigraphic order, indicating that the ages not only record the time of eruption but also that deposition occurred very shortly after eruption. The isotopic dating results already available mean that fossils can usually be assigned ages to better than 0.1 Ma, without further direct dating, provided that the fossils can be placed within the stratigraphic sequence of tuffs.

Alkali feldspar crystals were initially separated in 1978 from pumice clasts in a number of the tuffaceous beds in the Koobi Fora region and K/Ar ages were measured on multigrained samples (McDougall et al. 1980; McDougall 1985, 2014). Subsequently this was followed by $^{40}\text{Ar}/^{39}\text{Ar}$ step heats on selected multigrained samples (McDougall 1981, 1985) and then by multiple single-crystal $^{40}\text{Ar}/^{39}\text{Ar}$ total fusion analyses (McDougall and Brown 2006, 2008; McDougall et al. 2012), yielding essentially concordant results. The fluence monitor used in the earlier step-heating experiments was GA1550 biotite with K/Ar age of 97.9 Ma (McDougall and Roksandic 1974; Steiger and Jäger 1977), although with a revised K content, the K/Ar age is now given as 98.5 ± 0.5 Ma (McDougall and Wellman 2011). The step-heating experiments all yielded essentially flat age spectra, providing increased confidence that the derived ages are those of the igneous eruption and have not been subsequently disturbed (Lee 2014). The single-crystal $^{40}\text{Ar}/^{39}\text{Ar}$ ages are reported versus the Fish Canyon Tuff sanidine (FCs) fluence monitor age of 27.8 Ma, although subsequently we used 28.1 Ma for its age (Spell and McDougall 2003). Figure 2 shows the recent single-crystal results on the alkali feldspars from the volcanic-derived tuffs, and the concordancy of the results with the stratigraphy, younging upward (using the latter age for FCs), is striking.

The ages recorded at Kanapoi, southwest of Lake Turkana, are also on alkali feldspar. These ages were initially reported by Leakey et al. (1995, 1998) and were recalculated by McDougall and Brown (2008) using the slightly greater age of 28.1 Ma for the Fish Canyon Tuff sanidine (FCs) fluence monitor. The significance of these rather precise ages is that many fossil hominins assigned

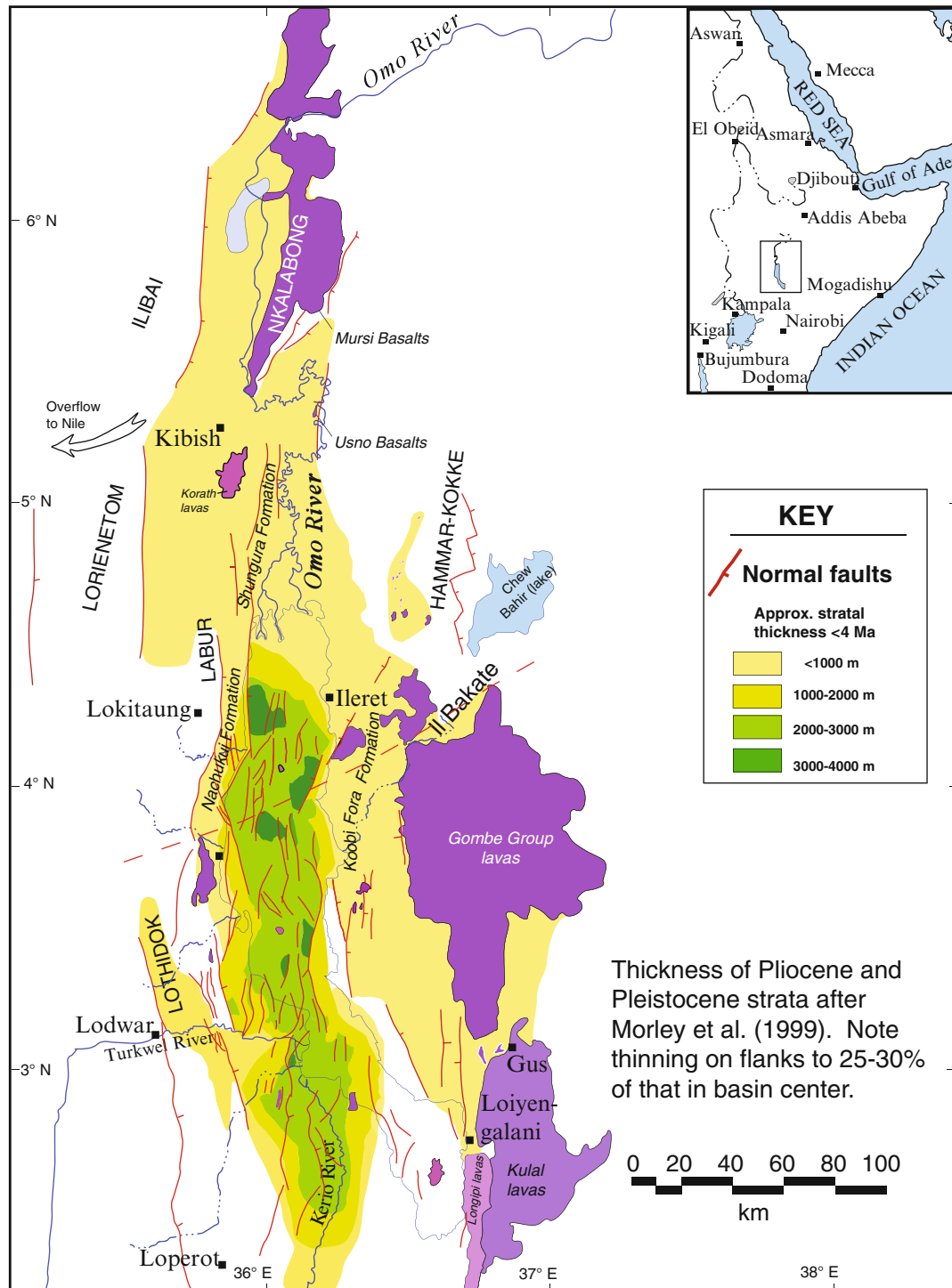


Fig. 1 Distribution and thickness of Omo Group sedimentary sequences in the Omo-Turkana Basin from interpretation of seismic data and from measured stratigraphic thicknesses. Principal areas of outcrop of the Shungura, Nachukui, and Koobi Fora formations are shown with diagonal shading. Inset shows the location of the map in northeast Africa (Diagram produced by F. H. Brown and published in McDougall et al. (2012))

to *Australopithecus anamensis* were found in this stratigraphic section, mainly below the Kanapoi Tuff, so their age is very tightly controlled between about 4.2 and 4.1 Ma. However, Leakey et al. (1995, 1998) also included hominin fossils of this species from Allia Bay, on the east side of

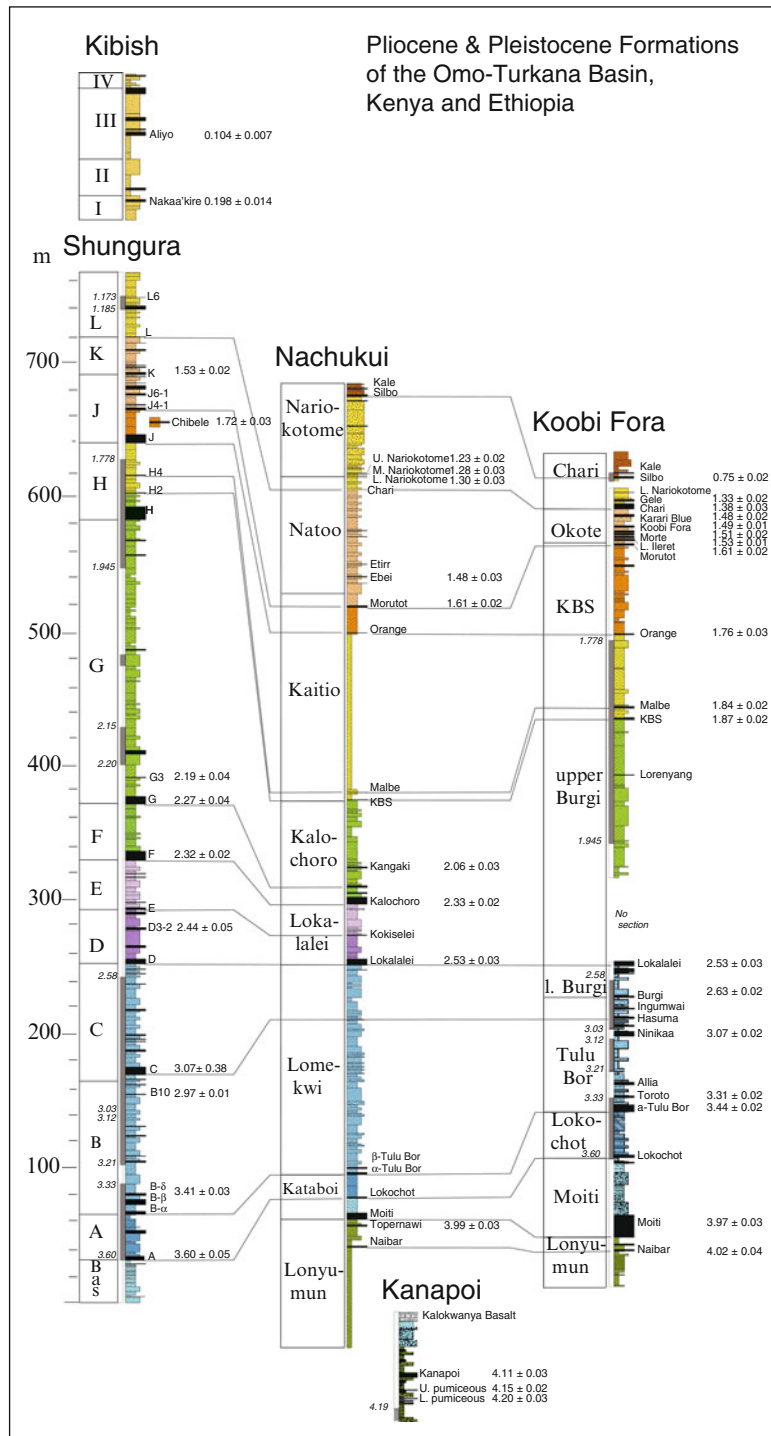


Fig. 2 Composite stratigraphic sections of the main formations in the Omo-Turkana Basin, together with the results of $^{40}\text{Ar}/^{39}\text{Ar}$ dating of mainly alkali feldspar from pumice clasts within tuffs, where the quoted error is the standard deviation of the population (McDougall and Brown 2006, 2008; McDougall et al. 2012). The main tuffaceous beds are shown, often named, and correlations between the stratigraphic columns are indicated by linking lines (Diagram drawn up by F. H. Brown, slightly modified from that in McDougall et al. (2012)). To the left of the stratigraphic columns for the Koobi Fora and Shungura formations are the measured magnetic polarities, where gray shading represents normal polarity and unshaded indicates reversed polarity. Ages assigned to the polarity boundaries are from Gradstein et al. (2012). For the dating, the Fish Canyon Tuff sanidine fluence monitor was assigned a reference age of 28.1 Ma (Spell and McDougall 2003)

Lake Turkana, where they are shown to be just below the Moiti Tuff, which has been dated at 3.97 ± 0.03 Ma, thus extending the age range for *A. anamensis* significantly.

About 100 km to the north of Lake Turkana, the Kibish Formation was deposited between about 200 ka and nearly the present time (McDougall et al. 2005, 2008; Brown and Fuller 2008). Four members were defined in the Kibish Formation, each reflecting a very high stand of Lake Turkana at the time of deposition, with Members I to III showing evidence of having been deposited in deltaic environments, whereas the youngest member, Member IV, is thought to have been formed as a lake margin deposit, during the Holocene. Each of the members was deposited over very short intervals, with much of the time represented by the disconformities usually evident between members. From Member I several hominin fossils were recovered in the original expedition to the region. Leakey (1969) and Day (1969) described two of these crania as belonging to somewhat archaic *Homo sapiens*. The more recent expeditions to the region confirmed the provenance of these fossils and also were able to $^{40}\text{Ar}/^{39}\text{Ar}$ date alkali feldspar from the Nakaa'kire Tuff from just below the level of Omo II, one of the fossil hominins. The age of the tuff was determined to be 198 ± 14 ka or ± 2 ka, where the latter error quoted is that for the weighted mean age. It was argued by McDougall et al. (2005, 2008) that this age was very close to that of hominin Omo II, because of the deduced rapid deposition of each member and because there was a quite unexpected correlation with deposition of sapropel 7 in the Mediterranean Sea, some 3,000 km to the northwest. The link was that high lake levels required for deposition of the members of the Kibish Formation as delta deposits of the earlier Omo River, some 100 km north of the present Lake Turkana, was brought about by very high rainfall in the Ethiopian Highlands, the source of the Omo River and the Blue Nile, and this resulted in overflow of Lake Turkana across the divide into the White Nile. These very large flows of the Nile River system were implicated in the formation of the sapropels in the Mediterranean Sea (Rossignol-Strick et al. 1982). In Member III of the Kibish Formation occurs the Aliyo Tuff, from which small pumice clasts yielded alkali feldspar crystals that were also dated, yielding a mean age of 104 ± 7 ka (Fig. 2) or ± 1 ka if the error is that of the weighted mean age. This age is consistent with its stratigraphic position and also shows that the hominins Omo I and II are older than this. The age of Omo I and II is regarded as close to 195 ka, the oldest presently known occurrence of *Homo sapiens*.

Results from Afar, Ethiopia

Studies in the Afar region of Ethiopia have been of significance and most helpful in providing age constraints on the many hominin fossils recovered from these sequences that range in age from Miocene to Pleistocene. The sequences have produced a prolific vertebrate fauna, including fossils assigned to a number of hominins; these include *Ardipithecus ramidus* (White et al. 1994, 1995), *Australopithecus afarensis* (Johanson et al. 1978, 1982; Johanson and White 1979), and *Homo sapiens* (White et al. 2003), among others. The sedimentary rocks occur over a wide region, with geological and palaeontological studies concentrated in particular areas. Space does not permit a review of the results (see McDougall 2014), but many hominin species are in the range 5.6–3.1 Ma and younger, through many interbedded volcanically derived tuffs, etc., dated by the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, with ages concordant with the stratigraphic order (Renne et al. 1999; Walter 1994). The *Homo sapiens* at Bouri has an age between about 154 and 160 ka (Clark et al. 2003).

Conclusions

In this contribution, a review of the place of K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating has been made in relation to youthful volcanic rocks and related products and how these results have provided well-constrained ages for a wide range of hominin fossils, especially those recovered from sites in East Africa. In the majority of cases, this has enabled workers to place hominin fossils in an independent time scale, unrelated to the perceived evolutionary stage exhibited by the fossils. It has been stressed that most numerical ages assigned to hominins and other vertebrates are from interpolation between dated igneous-derived samples rather than by directly dating the fossils themselves. Especially with continued development of the $^{40}\text{Ar}/^{39}\text{Ar}$ technique, the results generally have become well accepted by the geological and paleoanthropological community.

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